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SELECTIVE IDENTIFICATION OF OLEFINS AND PARAFFINS IN MIDDLE DISTILLATES OF SYNTHETIC CRUDE OIL

Final Report

by

H. Notzl

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MEMORANDUM

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****

SUBJECT: OSQ84-00433 SELECTIVE IDENTIFICATION OF OLEFINS AND PARAFFINS IN MIDDLE DISTILLATES OF SYNTHETIC CRUDE OIL

Please note that pp. 150-199 are not missing. That section containing NMR spectra is only an appendix whose page numbering has no relation to the page numbering of the main text of the final report. The "missing pages" of the appendix contained NMR spectra that had to be redone because of inconsistencies. They were not included in the final report but the page numbers were not updated.

I hope that this will satisfy your concerns.

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1. SUMMARY

The objective of this program was to assess methods needed to characterize the 160°C-340°C distillate fractions. The methods were evaluated using materials originating from thermal processing of bitumen, thermal recovery of heavy oil and coal liquification in order to determine how the methods handled the different distillates.

The characterization included chemical composition by a variety of techniques including low resolution mass spectrometry, gas chromatography, gas chromatographic mass spectrometry, infrared spectroscopy, nuclear magnetic resonance spectroscopy and physical characteristics.

The work showed that both the hydrocarbon composition and physical properties varied significantly depending on the origin. The methods, in most cases, gave very consistent results. As boiling ranges varied, widely direct comparison of the other properties should be carried out with caution.

For any future work, the materials should be distilled to a constant boiling range and engine tests performed to ascertain diesel engine performance.

2. INTRODUCTION

The purpose of this project was to characterize (with a series of methods) the diesel fuel fraction (160°C to 340°C) produced from the thermal processing of bitumen, heavy oils and residues. Coking of bitumen by Syncrude or Suncor processes, fireflooding of heavy oils for in situ oil recovery and coal liquifaction were processes which produced middle distillates with unique chemical compositions. These distillates could be used as a diesel fuel if specifications such as distillation, cetane index (and number), density and aromatics content were met.

This project was initiated to:

1. Determine olefin and paraffin content in diesel fuel from these different processes.
2. Provide insight into the effect hydrocarbon composition has on ignition properties of diesel fuel via cetane index.

The procedures used to determine the composition included:

1. Physical Characterization by ASTM Procedures
2. Hydrocarbon Separation: Saturates
   Aromatics
   Resins
3. Paraffin Content: n-Paraffin
   iso-Paraffin
4. Olefin Content
5. NMR, GCMS and IR

Some of the methods originally proposed were not successful in characterizing the distillates and therefore methods had to be developed.

3. BACKGROUND

Thermal processing of bitumen, heavy oils and coal produce many hydrocarbon species not normally found in conventional crudes. Diesel fuel from conventional crude does not contain olefins however diesel components produced by coking contain large amounts of olefins which can lead to performance problems in an engine.

The seven distillate samples analysed in the following report originated from different refinery processes and therefore, have varying hydrocarbon compositions (e.g. olefin content).

1. Suncor Coker Kerosene
2. Suncor Hydrotreated Light Gas Oil
3. Husky Fireflood
4. Wyodak Liquified Coal
5. Commercial Diesel
6. Syncrude Effluent Flash Vacuum Liquid
7. Edmonton Coker Distillate

Of the seven samples, only one distillate [commercial diesel (5)] was obtained by the conventional refinery distillation of crude oil. Since no processing other than distillation was used, the commercial diesel should be a highly saturated non olefinic distillate.

The different coking processes listed above (Syncrude, Suncor, Edmonton) produced distillates of varying hydrocarbon compositions including olefins not found in conventional crude distillation.

The Edmonton coker kerosene was produced by coking conventional crude heavy ends (VTB). The other two coking processes (Suncor and Syncrude) were sources for the other three samples.

1. Suncor Coker Kerosene
2. Syncrude EFV O/H, and
3. Suncor Hydrotreated (HT) Light Gas Oil (LGO)

These two processes (Suncor and Syncrude) use a hot caustic solution to extract bitumen from tar sand followed by

(1) delayed coking of recovered bitumen for Suncor, or
(2) fluid coking of recovered bitumen for Syncrude upgrading.

The Husky Fireflood sample was obtained from in situ oil recovery fireflood system while the Wyodak liquified coal distillate was from a coal upgrading process.

All seven of the above distillate samples differ from each other in origin and are expected to vary in hydrocarbon composition (e.g. saturates, aromatics) and physical characteristics (e.g. cetane index, distillation). It is these compositional differences which will be determined and compared in this project.

4. EXPERIMENTAL PROCEDURES

Seven samples, four from CANMET and three from Petro-Canada, were analysed for their physical characteristics and hydrocarbon classification for the 160°C to 340°C boiling range.

Two of the seven samples Husky Fireflood (AP3) and Wyodak Liquified Coal (AP4) required distillation on a 15 plate (2:1 reflux ratio) glass distillation column to obtain the 160°C to 340°C boiling range needed before further testing could be done.

Figure 4.1 summarizes the experimental procedures followed and discussed below.

4.1 Physical Characterization

Physical characteristics such as density, boiling point, viscosity, and cetane indices were determined on the seven middle distillate fractions. The American Society for Testing and Materials (ASTM) procedures were:

4.1.1 Density ASTM D4052

The density or relative density (relative to air) of middle distillates was determined by a PAAR densimeter at a temperature of 15°C. The change in oscillating frequency caused by change in mass of the tube before and after sample addition was used in conjunction with calibration data to obtain sample density (g/cc).

4.1.2 Aniline Point ASTM D611

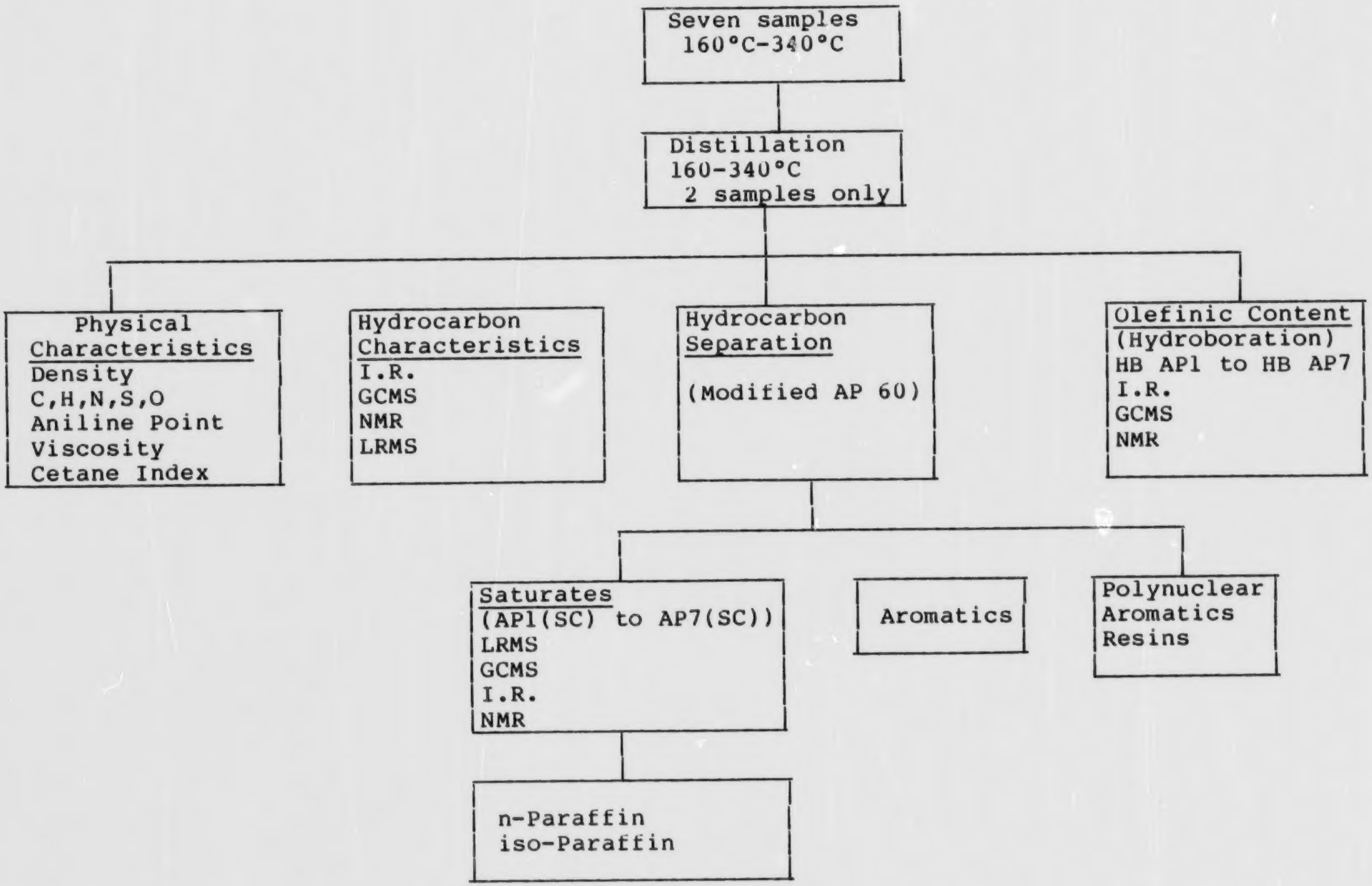
Aniline point was the minimum equilibrium solution temperature for equal volumes of aniline and sample, and is most often used to estimate aromatic hydrocarbon content of mixtures.

4.1.3 Viscosity ASTM 445

The kinematic viscosity of distillate fractions was determined by measuring the time for a volume of liquid to flow under gravity through a calibrated glass capillary viscometer.

FIGURE 4.1

SUMMARY OF EXPERIMENTAL PROCEDURES


Seven samples
160°C-340°C
Distillation
160-340°C
2 samples only
Physical Characteristics
Density
C,H,N,S,O
Aniline Point
Viscosity
Cetane Index
Hydrocarbon Characteristics
I.R.
GCMS
NMR
LRMS
Hydrocarbon Separation
(Modified AP 60)
Olefinic Content
(Hydroboration)
HB AP1 to HB AP7
I.R.
GCMS
NMR
Saturates
(AP1(SC) to AP7(SC))
LRMS
GCMS
I.R.
NMR
Aromatics
Polynuclear Aromatics Resins
n-Paraffin
iso-Paraffin

4.1.4 Distillation ASTM D86

The one plate distillation determined the volatility characteristics of distillate fractions.

4.1.5 Cetane Index ASTM D976

The density (D4052) and boiling range (D86) was used to calculate a direct "Estimate" of the ASTM cetane number.

The sample volume was too small for an engine rating therefore an approximate cetane number was calculated.

4.1.6 Cetane Index (CGSB)

The Canadian Government Standards Board (CGSB) has another cetane number correlation similar to the ASTM 976 Cetane Number which used aniline point (D611) and viscosity (ASTM 445) as well as density (ASTM 4052) and distillation (D86).

CGSB Cetane Index (CI)

$$\begin{aligned} CI = {} & 77.7628 + 0.1765\ AP + 0.003867\ AP^2 \\ & - 11.6150\ K_c + 0.5844\ K_c^2 - 0.635V \end{aligned}$$

where: AP = Aniline Point °C
V = Viscosity @ 40°C, cSt
D = Density @ 15°C, g/mL
T = Temperature °C from D86

$$K_c = \frac{10\%\ T + 50\%\ T + 90\% + 820}{(200)\ (D^2)}$$

4.1.7 Nitrogen

The total nitrogen was determined by chemiluminescence.

4.1.8 Sulfur Content: CANMET

The sample was irradiated with an x-ray beam and the intensity of the sulfur Kα line at 5.37Å was measured. The resultant net counting rate (sample background) was compared to a calibration curve to obtain the weight percent sulfur in distillate samples.

4.1.9 Carbon Content: CANMET PE-240

4.1.10 Hydrogen Content: CANMET PE-240C

4.1.11 Oxygen Content: CANMET PE-240

4.1.12 Average Molecular Weight - GCD

Gas chromatographic distillation (GCD) was used to determine average carbon number distribution and hence average molecular weight.

4.2 Hydrocarbon Separations

The seven middle distillate samples were separated into saturates, monoaromatics, polynuclear aromatics and resins using a modified U.S. Bureau of Mines procedure API project No. 60. The method used low pressure liquid chromatography to separate the four hydrocarbon classifications and enough sample of each fraction was produced for further testing described in Sections 4.3 to 4.8.

The chromatographic column was a 1.27 cm OD (0.94 cm OD) 316 stainless steel tube with a length of 137 cm. The lower half of the column was packed with 37 g of Davidson Grade 12 (28-200 B.S. mesh) silica gel which had been activated at 250°C for 20 hours. The top half of the column was packed with 47 g of Alcoa F-20 (80-200 B.S. mesh) alumina activated at 400°C for 20 hours. The unfilled spaces at both ends of the column were plugged with glass wool.

To remove adsorbed oxygen from the packing, pentane was pumped (Waters HPLC pump) from a solvent reservoir and through the column overnight. At the beginning of the test, the n-pentane flow rate was adjusted to 5 mL/min and a sample of middle distillate (1.4 g) was introduced through a septum at the bottom of the column. The saturate fraction, eluted by the n-pentane, was collected from the top of the column in a 500 mL glass bottle. The solvents used for hydrocarbon elutions were:

Solvent	Volume (mL)	Hydrocarbon Separation
n-pentane	330	Saturates (SC)
10% toluene in pentane	500	Mono and diaromatics (MA)
5% ethyl acetate in toluene	130	Polynuclear aromatics (PNA)
Methanol	200	)
Toluene	100	) Resins (R)
n-pentane	100	)

After sample elution, the solvent was evaporated off each of four fractions using a Rotavapor R110. To remove n-pentane with minimum sample loss, ice and minimum vacuum was used. The toluene in both the mono-diaromatics and polyaromatics fractions was azeotropically removed by mixing the sample with methanol. Heat was added when needed on all fractions except the saturates.

One middle distillate sample was separated a minimum of three times to:

1. Obtain enough sample for further testing
2. Confirm procedure repeatability

On confirmation of a greater than 85 wt.% mass balance (i.e. total weight of fractions divided by initial sample weight), the saturates and mono-diaromatics were analysed by low resolution mass spectrometry (LRMS) to determine composition and recalculate hydrocarbon composition for comparison with feed data (Appendix I).

The three saturate fractions (S) for each sample were mixed to provide a combined saturate fraction (SC) for n-paraffin and iso-paraffin determinations by Gas Chromatography (GC) and Gas Chromatography Mass Spectrometry (GCMS).

4.3 Low Resolution Mass Spectrometry (LRMS)

Middle distillate samples as well as saturate and aromatic fractions from the hydrocarbon separation procedure were analysed on a Kratos 25Q Low Resolution Mass Spectrometer using the Robinson method (G.J. Robinson, Low Resolution Mass Spectrometry Determination of Aromatics and Saturates in Petroleum Fractions, Analytical Chemistry 43, 11, Sept. 1971).

4.4 N-Paraffin Determination by Gas Chromatography (GC)

The seven saturate fractions [AP 1(SC) to AP7(SC)] obtained from the hydrocarbon separation (Section 4.2) were analysed for their n-paraffin content by high resolution gas chromatography according to the procedure of H. Obbens and L. Huber (Hewlett-Packard Application Note AN 228-34) and B.T. Hine, Chromatographia 18 (1984), 679.

The original contract requested the use of molecular sieve absorption (Sista, V.R. and Srivastava, G.C. Analytical Chem, 48 (1987) 1582) to separate saturates into n-paraffins and iso-paraffins. However, this method did not work for the middle distillates samples (Appendix IIA).

4.5 Olefin Content by Hydroboration

Each of the seven distillate composite samples was hydroborated by the anti-Markovnikov addition of diborane to the olefinic bond (M.A. Poirier and A.E. George, Fuel, 60(1981), 194 and Fuel, 61(1982), 182). A 25 mL aliqnot of dry ethyl ether was introduced into a 250 mL, three neck round bottom flask equipped with a magnetic stirring bar, a condenser and a dropping funnel. Approximately 2.2 g of distillate was added to the flask, the stirrer turned on, and the system purged with nitrogen. An ice bath cooled the mixture and once 0°C was maintained, 2 mL of (excess) of borane-methyl sulphide complex (i.e. n in BH_3) was added dropwise through a septum. The solution was stirred at room temperature for 1.5 hours. After refluxing, the reaction mixture was cooled to 0°C and 15 mL of 3N sodium hydroxide was slowly added, followed by 15 mL of 30% hydrogen peroxide solution. The reaction mixture was transferred to a 250 mL separating funnel, diluted with 100 mL of ether and washed four times with 100 mL of saturated NaCl solution. Two 100 mL water washes were then performed and the ether phase was dried over anhydrous sodium carbonate. The ether solution was filtered and the solvent removed by evaporation in a fumehood.

The hydroborated (HB) samples were analysed by infrared, GCMS and NMR to determine the alcohol distribution and hence the olefin content. The extraction methods and gravimetric determination of olefins suggested in the procedure were not followed because of light end losses of samples with IBP <200°C (Appendix IIA). Instead, infrared identification of the OH at 3610 cm^{-1} was used to determine the alcohol content (J. Chmielowiec, "Characterization of Light Instability Precursors in Hydrotreated Gas Oil").

4.6 Gas Chromatography - Mass Spectrometry (GCMS)

The GCMS data for the seven composite samples (AP1 to AP7), the seven saturate fractions [AP1 (SC) to AP7 (SC)] and the seven hydroborated samples (HB AP1 to HB AP7) were obtained using a combined capillary gas chromatograph (30 m, 0.32 mm I.D., 1 m wall-coated re-silicone) and EI - LRMS. Quantitation was completed with a DS-55/GCQUAN software package. DS55 is a software package for the Data General Eclipse computer that was developed by KRATOS, Manchester, England. The software permits digitisation and time-to-mass conversion of analog mass spectral signals and further processing of the acquired data, KRATOS' programs "Datac", "Plot", "GCQUAN" and "XSCAN" were used extensively to digitise, plot and quantitize raw data and generate the results for this work project.

4.6.1 GCMS Composite Analyses (AP1 to AP7)

The total ion current traces (TIC) and the molecular ion plots (Appendix II) were produced, GCMS data were peak averaged and semi-quantitative compositional analyses (similar to LRMS Robinson analyses) were computed.

4.6.2 GCMS Saturate Analyses [AP1 (SC) to AP7 (SCC)]

The normal paraffins (n-paraffin) and iso-paraffins were identified by plotting peak ion summations for E_{43} and E_4 followed by baseline drawing and subsequent quantitation.

4.6.3 GCMS Olefin Analyses

The alcohol content of hydroborated samples was difficult to elute from the GC column. Therefore, alcohols were converted to the trimethyl silylate (TMS) using TMS reagent (20 TMS-reagent:1 distillate). The excess TMS reagent was hydrolysed to prevent column damage by the TMS reagent, and the distillate material was hexane-extracted from the aqueous phase. Controlled evaporization removed the volatile hexane.

The TMS ethers were determined by their characteristic ions at m/e 73 $(-Si-(CH_3)_3)^+$) and m/e 75 $(-O-Si-(CH_3)_3H^+)$ as well as their associated molecular ions. The concentration of the TMS ethers were established based on the typical characteristic intensity of m/e 73 or 75 over the total ionic current (TIC) envelope. These GCMS estimated concentrations relate back to the hydroxyl content of the hydroborated samples and therefore the olefin content in the original sample.

4.7 Infrared Analyses

Seven combined samples (AP1 to AP7), seven saturate fractions [AP1 (SC) to AP7 (SC)] and seven hydroborated samples (HB AP1 to HB AP7) were scanned between 4000 cm^{-1} and 200 cm^{-1} using a Model 283B Perkin Elmer.

4.8 NMR Analyses

The H Nuclear Magnetic Resonance (NMR) spectra of the twenty-one samples were recorded at 399.869 MHz on a Varian XL-400 Spectrometer. The spectra were acquired in 32-64 scans over a sweep width of 400 Hz (3.752 s acquisition time). Spectra were acquired in 32K data points and a 1.0 s delay was used between each acquisition. The free induction delays were processed without the application of any weighing functions and were zero-filled to 64K.

Carbon 13 spectra obtained at 100.559 MHz were recorded over a 20.0 KHz sweep width in 32K data points (0.750 s acquisition time) and a 1.0 s delay was used between each acquisition. The spectra were acquired in 500-1500 scans and data were processed with the application of an exponential weighing function producing a 1.0 Hz line broadening, and were zero-filled to 64K.

5. RESULTS AND DISCUSSION

Seven hydrocarbon fractions were analysed for their saturate (n-paraffin), aromatic (mono and diaromatic), and olefin content using the procedures discussed in the Experimental Section. The seven samples analysed were:

AP1/Suncor Coker Kerosene
AP2/Suncor Hydrotreated Light Gas Oil
AP3/Husky Fireflood
AP4/Wyodak Liquified Coal
AP5/Commercial Diesel
AP6/Syncrude Effluent Flash Vacuum (EFV)
AP7/Edmonton Coker Distillate

All samples except the Husky Fireflood (AP3) and Wyodak Liquified Coal (AP4) had hydrocarbon boiling range within the temperature range of 160°C to 340°C required in the contract.

The hydrocarbon composition and physical characterization for each of the seven samples is illustrated below. The Suncor coker kerosene (AP1) data is described in detail to interpret tables for the other six samples.

5.1 Suncor Coker Kerosene
(Combined feed = AP1, Saturate Fraction = AP1(SC) and Hydroborated Fraction = HB AP1)

Suncor coker kerosene was an olefinic distillate (195°C to 296°C) containing 13 wt.% paraffins (n-paraffins = 1 wt.%), 47 wt.% cycloparaffins, 32 wt.% aromatics and 8 wt.% resins. The n-paraffin content of 1 wt.% was derived from n-paraffin content of 8.1 wt.% (Table 5.1D) times paraffin content of 13 wt.% (Table 5.1B).

As a diesel fuel, the cetane index of the sample did not meet the specification of 40 but instead was low (34). This was not surprising due to the aromatics content of the Suncor coker kerosene.

Table 5.1A summarizes the American Society Testing and Materials (ASTM) methods and results used to physically characterize the distillate.

The hydrocarbon separation (Section 4.2) by solvent elution produced saturate and aromatic fractions which, when analysed by low resolution mass spectrometry (LRMS) and, recombined mathematically, (Appendix I) gave similar saturates and aromatics content.

These recombined analyses compared very well with the LRMS and GCMS data of original feed (Tables 5.1B and 5.1C). For example, in Table 5.1B the first and fourth columns are the LRMS and GCMS data on the original sample. The second column is the weight fraction produced by the solvent elution procedure (Section 4.2) resulting in the four hydrocarbon types:

1. Saturates
2. Mono-aromatics and di-aromatics
3. Polynuclear aromatics
4. Resins

The saturates and mono, di-aromatics fractions, (analysed by LRMS and the data recombined mathematical data) is given in the third column of Table 5.1B (Recalculated LRMS from Appendix I).

The hydrocarbon compositions (Tables 5.1B) resulting from the three procedures (LRMS, GCMS and hydrocarbon separation) are similar. Discrepancies in resin content seem to directly affect the cycloparaffin values.

The saturate fraction [API (SC)] recovered from the hydrocarbon separation procedure was analysed for paraffin content (Tables 5.1C and 5.1D.) The mass spectrometry data previously obtained in Tables 5.1B and 5.1C were recalculated to exclude aromatics (Table 5.1D) and interpret hydrocarbon composition for saturates only. The n-paraffin content, of 8.1 wt.% determined by both GC (Figure 5.1.1) and GCMS methods, gave similar n-paraffin carbon number distribution. By GCMS (Figure 5.1B Table 5.1C to 5.1D) the n- and iso-paraffins were identified by plotting peak ion summation for E_{43} and E_{41}, followed by baseline drawing and subsequent quantitation by the DS-55/GC QUAN software package.

The iso-paraffin content of saturate fraction [AP1 (SC)] determined directly by GCMS (Table 5.1D) of 5.1 wt.% was probably in error because of poor GCMS iso-paraffin quantitation and/or error in the Robinson matrix. This problem was illustrated by summing the normal and iso-paraffin determined in the original LRMS samples (19 wt.%) which does not match the iso- and n-paraffins found in the saturate fraction (13.2 wt.%).

The Suncor coker kerosene was olefinic as shown by the obviously olefinic band at 1640 cm^{-1} and 890 cm^{-1} (Figures 5.1D, 5.1E). Hydroboration (HB AP1) of the olefin to alcohol followed by an infrared scan (Figure 5.1F), as well as TMS reaction with GCMS ether analyses were two methods used to determine olefin content. By infrared, two distinct OH bands occurred at 3350 cm^{-1} and 1030 cm^{-1}. By GCMS, Figure 5.2C1 showed the total ion current (TIC) envelope and sum m/e 73 plus 75 ion plot. Figure 5.2C2 illustrated the m/e 228 to 312 TMS ether homologue that corresponded to C_{10} to C_{16} straight chain olefin (Z-0). A similar but less intense profile was observed for cyclic olefin (Z-2) and dicyclic olefin (Z-4). A three carbon number peak homologue at m/e 250, 236 and 222 suggests the transformation of m/e 134, 148 and 62 benzothiophenes to alcohols and subsequently TMS ether.

The GCMS TMS ether concentration (approx. 34%) was in good agreement with the olefin concentration from the bromine number of 38%. The alcohols by I.R. however were low compared to the other two methods (Table 5.1E).

The NMR data (Appendix III) also confirmed olefins, however the NMR aromatic content of 5.5 wt% did not agree with any of the LRMS, GCMS and hydrocarbon separation procedures. The NMR analyses interpreted aromatics and straight chain compounds in two distinct groups without considering highly branched aromatic molecules in the same way as mass spectrometry.

TABLE 5.1A

AP1 (COMBINED FEED) SUNCOR COKER KEROSENE PHYSICAL CHARACTERIZATION

Density at 15°C g/cc		0.8800
Aniline Point, °C (ASTM D611)		40
Cetane Index (ASTM D976)		34
Cetane Index (CGSB)		32
Nitrogen Content, ppm		414
Sulfur Content, wt%		2.5
Carbon Content, wt%		85.0
Hydrogen Content, wt%		12.1
Oxygen Content, wt%		0
Viscosity @ 40°C, ASTM D445 (cSt)		2.5
Distillation, ASTM D86, Vol.%		
°C (GCD wt.%)	IBP	195
	10	229
	20	238
	30	243
	40	246
	50	251
	60	255
	70	260
	80	266
	90	275
	FBP	296
Average Molecular Weight (GCMS)		190
Average Molecular Weight (GCD)		200

TABLE 5.1B

HYDROCARBON SEPARATION
AP1 (COMBINED FEED) SUNCOR COKER KEROSENE

		Separation		
Components	LRMS	Weight Fraction	Recal. LRMS	GCMS
	Wt.%	Wt.%	Wt.%	Wt.%
Saturates	67	62	60	74
Paraffins	13	-	13	14
Cycloparaffins	54	-	47	60
Aromatics	33	30	32	26
Mono-Di	27	28	25	22
Polynuclear	6	2	7	4
Resins	0	8	8	0

Weight % Aromatics in saturates fraction by LRMS 3.4 wt.%
Weight % Saturates in aromatics fraction by LRMS 1.3 wt.%

TABLE 5.1C

MASS SPECTROMETRY COMPOSITIONAL DATA
SUNCOR COKER KEROSENE
FEED (AP1) AND SATURATES [AP1 (SC)]

		Feed		Saturates	
	Z Numbers	LRMS	GCMS	LRMS	GCMS
Saturates		67	74	94	95
Paraffins	+2	12	14	21	21
Cycloparaffins		55	60	73	74
Noncond. Cycloparaffins	0	21	24	26	31
Cond. Dicycloparaffins	-2	19	22	29	27
Cond. Polycycloparaffins	-4	15	14	18	16
Aromatics		33	26	6	5
Monoaromatics		21	18	4	3
Alkylbenzenes	-6	8	9	4	3
Benzocycloparaffins	-8	7	5	0	0
Benzodicycloparaffins	-10	6	4	0	0
Diaromatics		6	4	1	1
Naphthalenes	-12	4	3	0	0
Naphthocycloparaffins	-14	0	0	0	0
Fluorenes	-16	2	1	1	1
Triaromatics	-18,-20	0	0	0	0
Tetraaromatics	-22,-24	0	0	0	0
Pentaaromatics	-26,-28,-30	0	0	0	0
Unidentified	-32 to -44	0	0	0	0
Aromatic Sulfurs	-105,-165,-225	6	4	1	1

TABLE 5.1D

PARAFFIN CONTENT
AP1 (SC)
MASS SPECTROMETRY DATA

Components	Feed		Saturates	
	LRMS	GCMS	LRMS	GCMS
Saturates	100	100	100	100
Paraffins	19	19	22	22
Cycloparaffins	81	81	78	78
Noncond. Cycloparaffins	31	32	28	33
Cond. Dicycloparaffins	28	29	30	28
Cond. Polycycloparaffins	22	20	20	17

	GCMS Wt.%	GC Wt.%	GC Wt.%
Normal Paraffins	8.1	8.1	-
Isoparaffins	5.1	-	-
Isoparaffins + Cycloparaffins (% Toluene)	-	0.2	91.9
Normal Paraffin Distribution Carbon Number			
C 9			
C10	0.1	0.1	0.2
C11	0.3	0.4	0.8
C12	0.9	1.1	3.9
C13	1.7	1.7	15.3
C14	2.1	1.8	21.3
C15	1.7	1.5	20.7
C16	0.8	1.0	18.4
C17	0.4	0.4	8.4
C18	0.1	0.1	2.6
C19	-	-	0.3

TABLE 5.1E

OLEFIN CONTENT
SUNCOR COKER DISTILLATE HB AP1

	HB AP1
Average MW (GCMS)	190
IR Wt.% OH	10
GCMS: wt. % TMS Ether	34
Bromine Number: wt.% Olefin	38

94 wt.% recovery of hydroborated sample

FIGURE 3.1.1

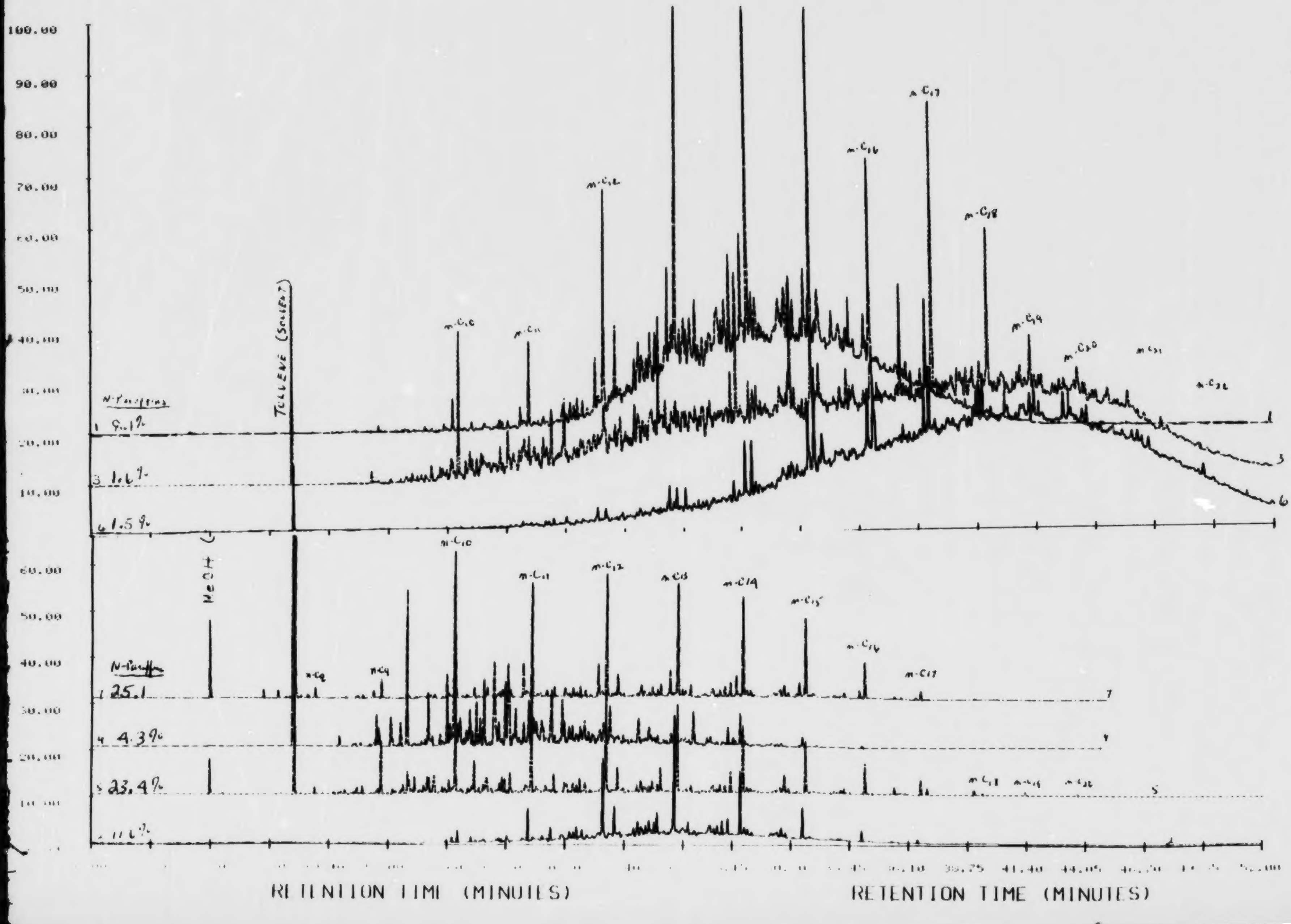
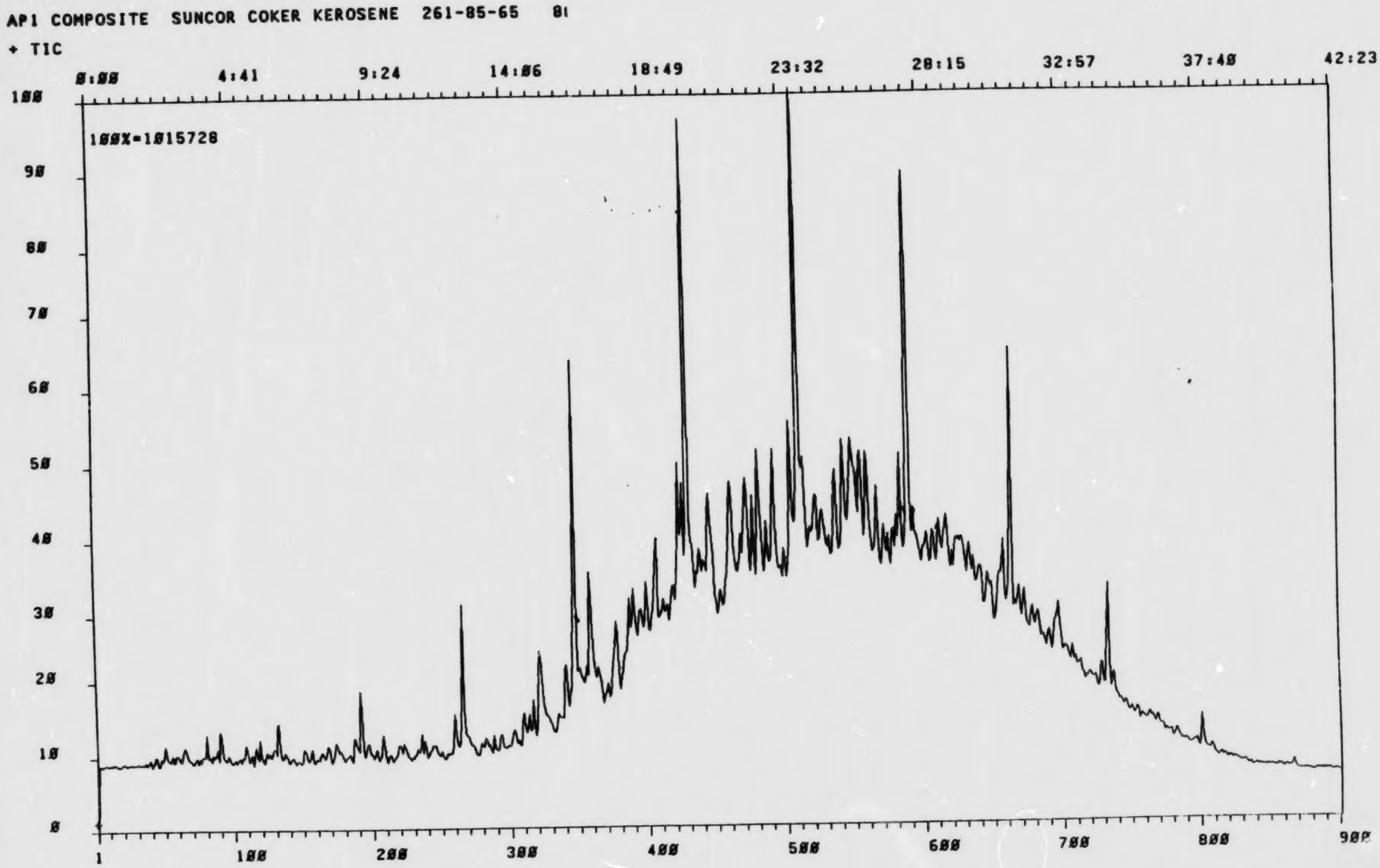

100.00
90.00
80.00
70.00
60.00
50.00
40.00
30.00
20.00
10.00
60.00
50.00
40.00
30.00
20.00
10.00
N-Paraffins
1 9.1%
3 1.6%
6 1.5%
N-Paraffin
1 25.1
4 4.3%
5 23.4%
2 11.6%
TOLUENE (SOLVENT)
MeOH
n-C8
n-C9
n-C10
n-C11
n-C12
n-C13
n-C14
n-C15
n-C16
n-C17
n-C18
n-C19
n-C20
n-C21
n-C22
1
3
6
7
4
5
2
36.10
38.75
41.40
44.05
46.70
52.00
RETENTION TIME (MINUTES)
RETENTION TIME (MINUTES)

FIGURE 5.1A


API COMPOSITE SUNCOR COKER KEROSENE 261-85-65 8
+ TIC
100%=1015728
0:00
4:41
9:24
14:06
18:49
23:32
28:15
32:57
37:40
42:23
100
90
80
70
60
50
40
30
20
10
0
1
100
200
300
400
500
600
700
800
900

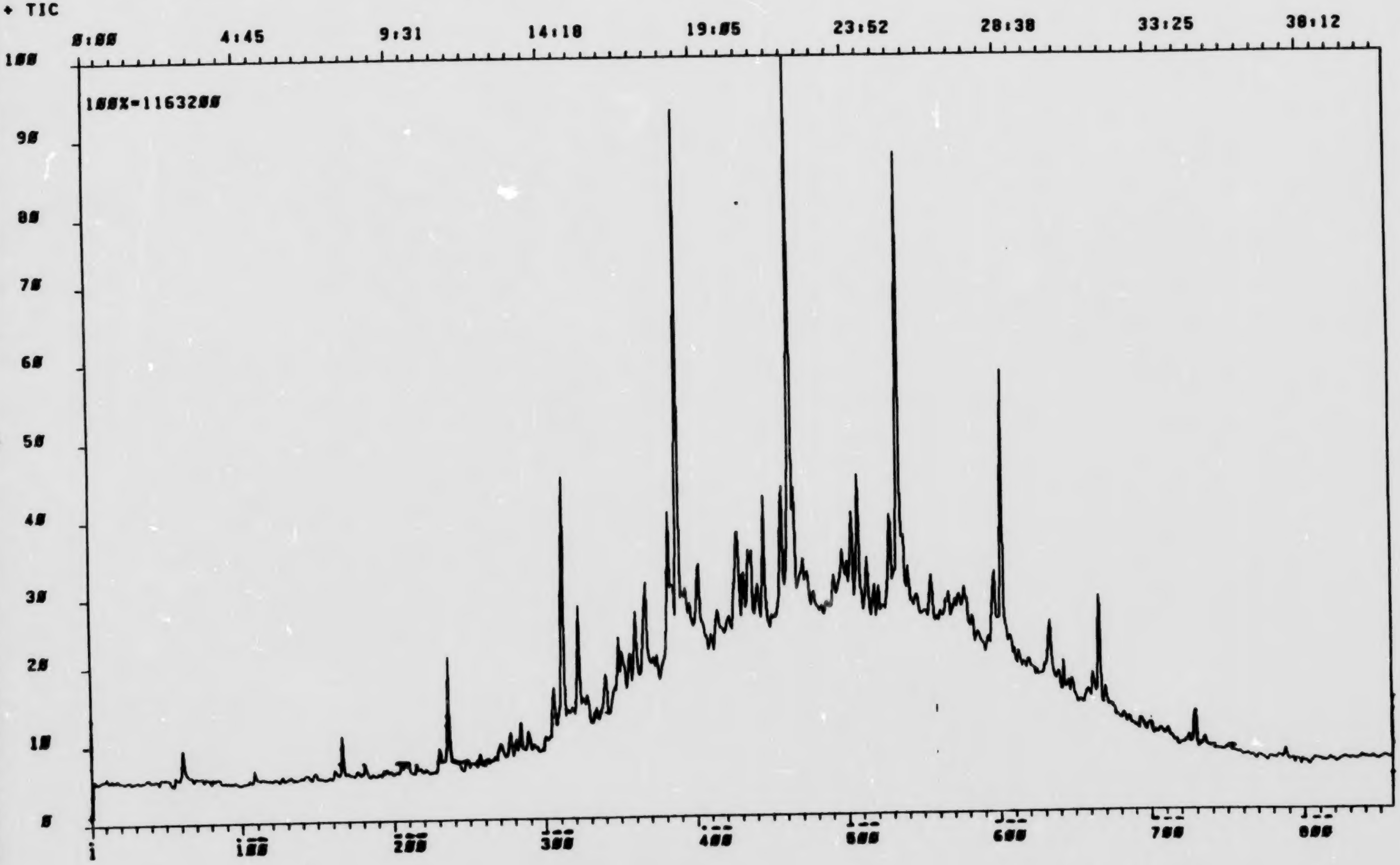
NAPHTHALENES

FIGURE 5

85-55 CROSS REPORT, RUN: 2F1033

API(SC) MID DIST SATS 261-85-65 860205

+ TIC

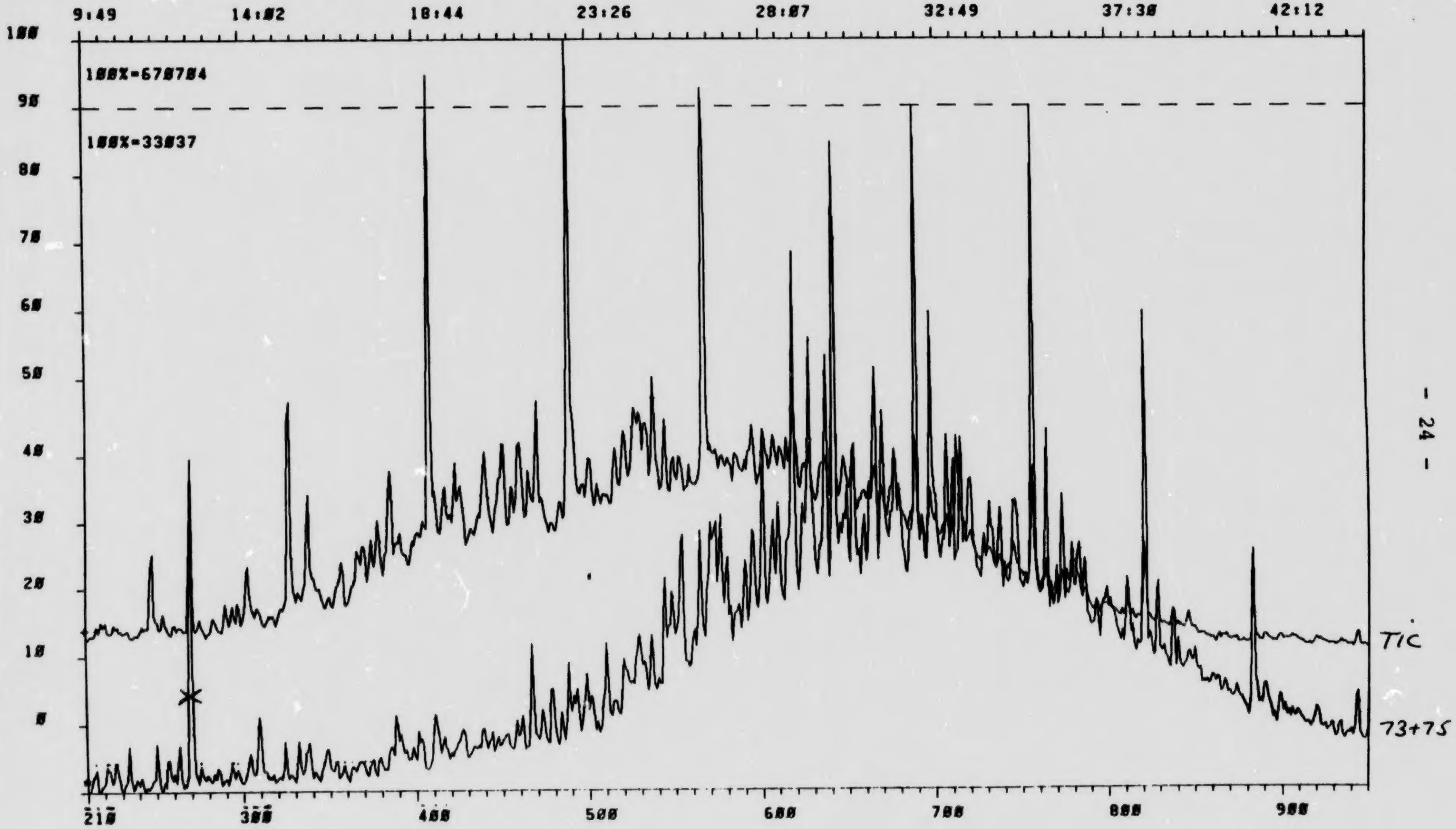


US-55 CROSS SCAN REPORT, RUN: 3F1059
HB1B SUNCOR COKER KEROSENE 261-85-65 860326
* 73 . 75 + TIC

FIGURE 5.1C1

Graph 1

5.2c -



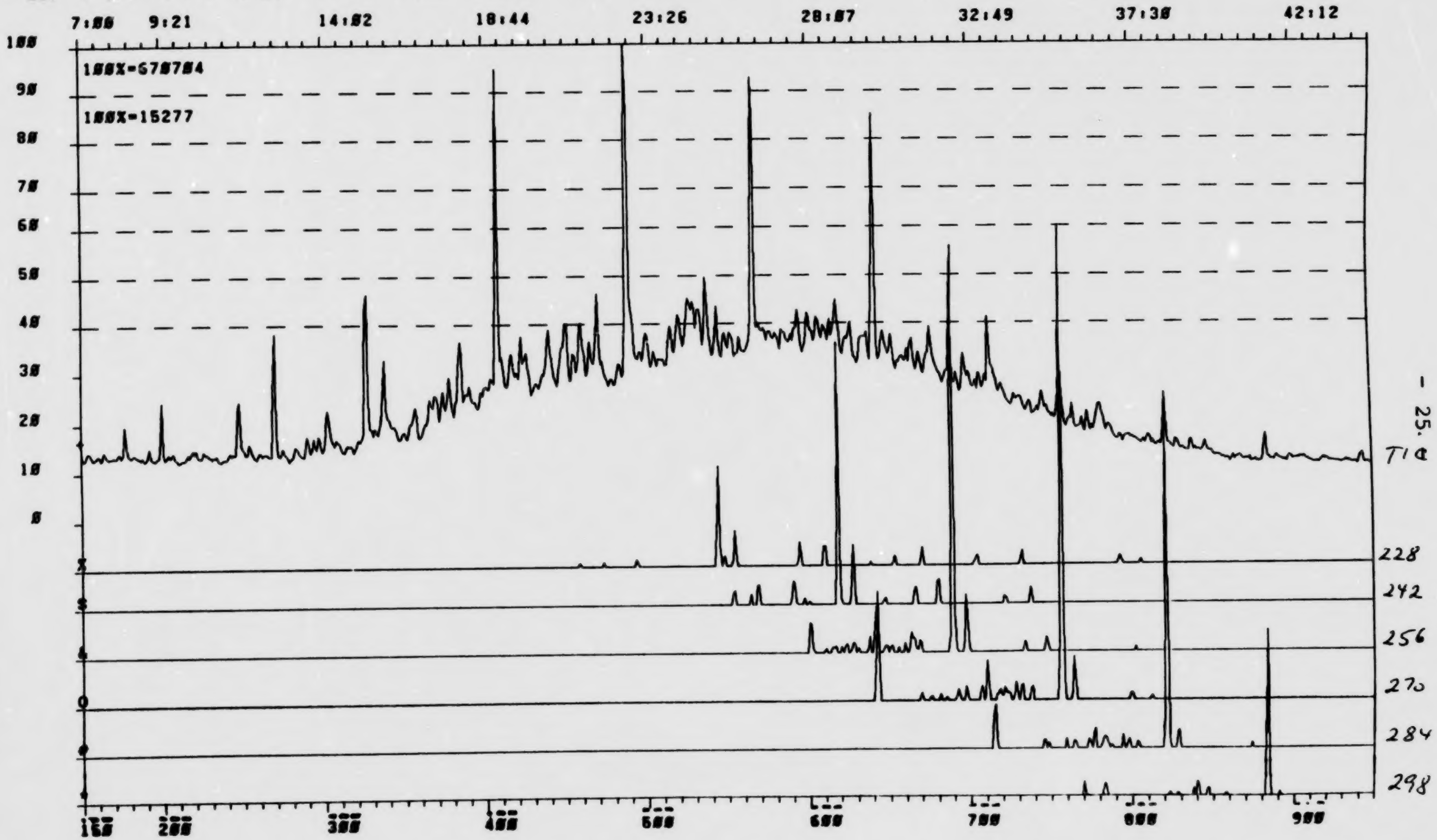
DS-55 CROSS SCAN REPORT, RUN: 3F1059

FIGURE 5.1C2

Graph 2

HB1B SUNCOR COKER KEROSENE 261-85-65 860326

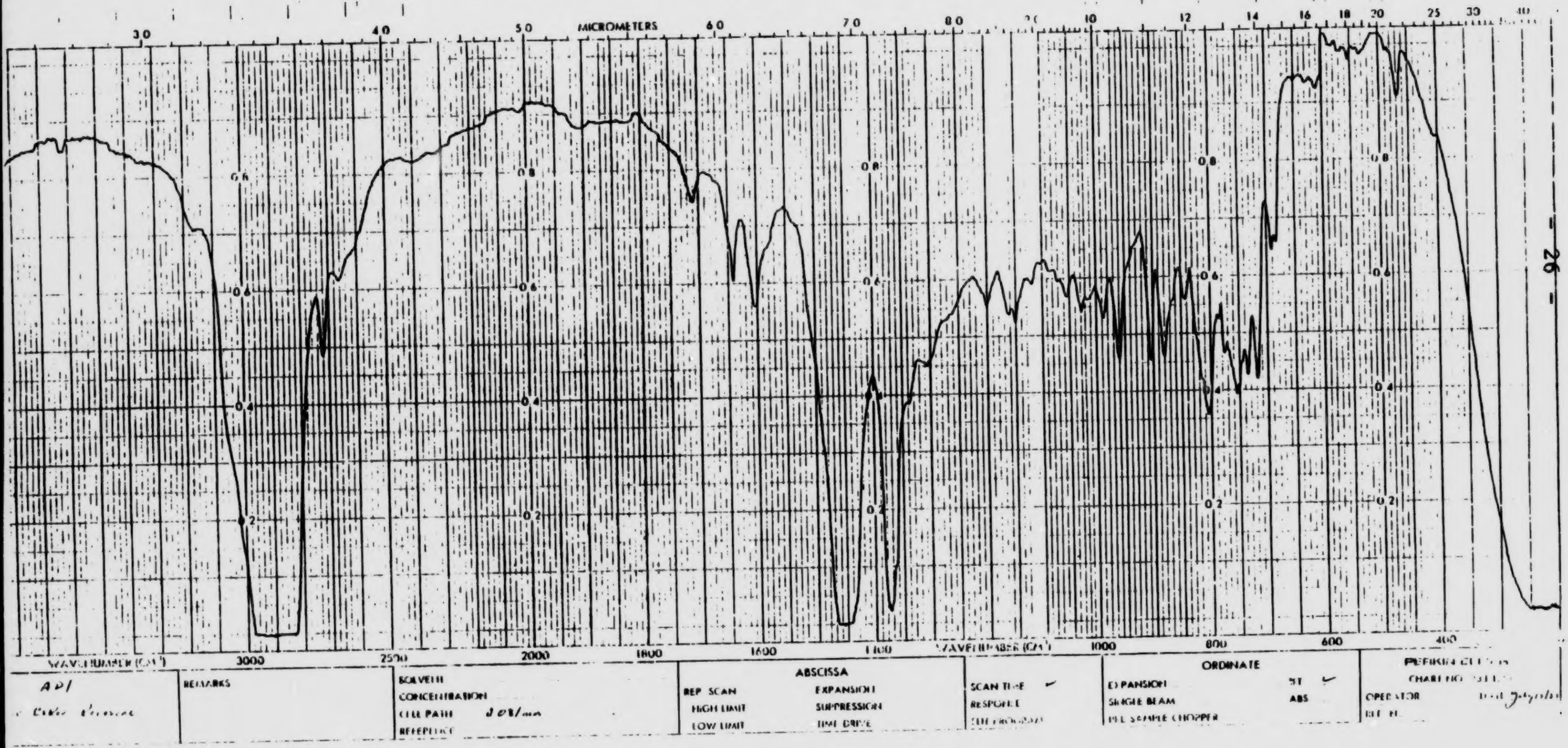
* 299 # 285 O 271 & 257 $ 243 X 229 + TIC (-1)



298 - 88 → 210 - C15/20 aliphatic monoolefins
284 196 - 14 "
270 182 - 13 "
168 - 12 "

FIGURE 5.1D

SUNCOR COKER KEROSENE
AP1
(SAMPLE AS IS)



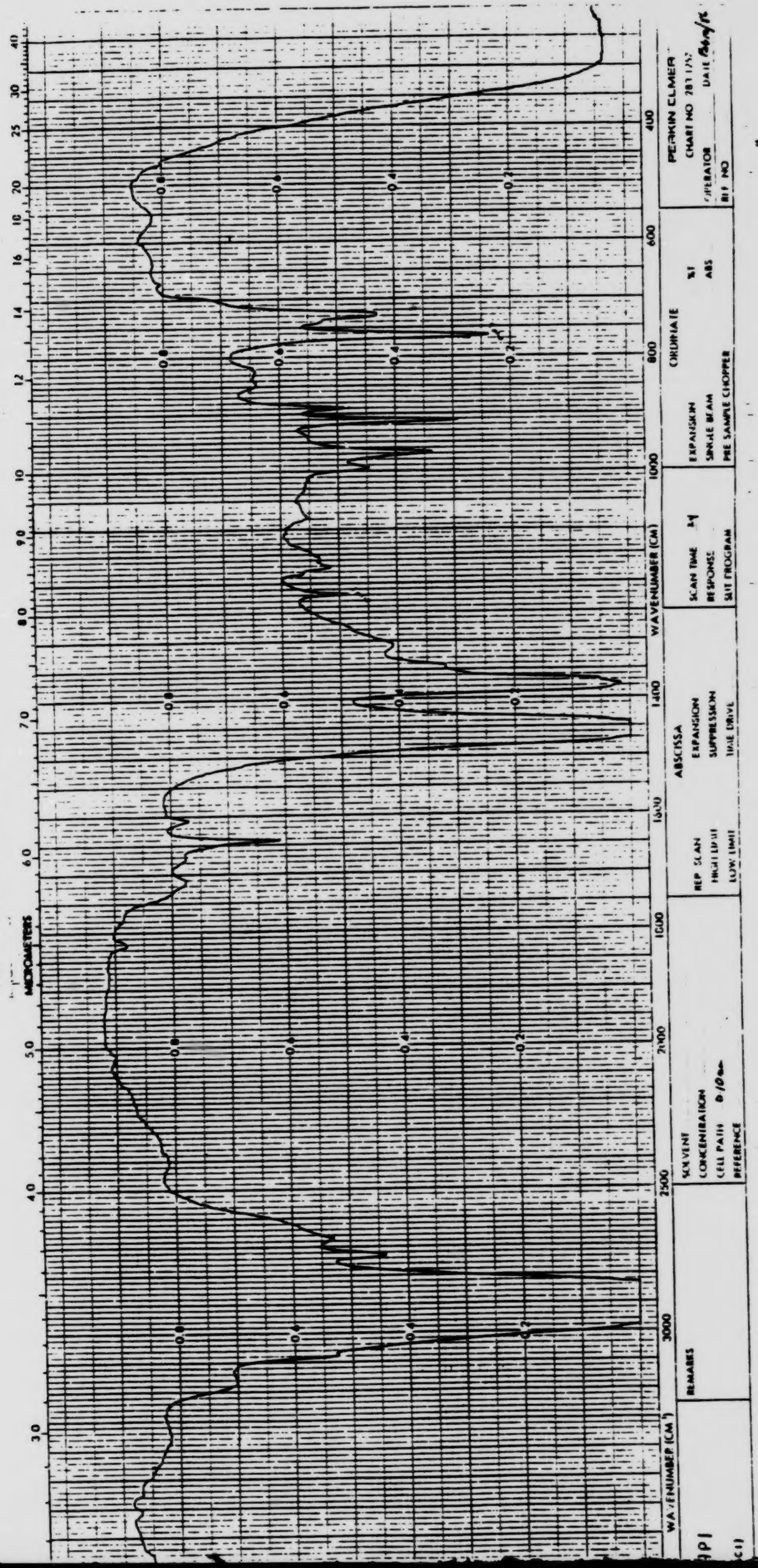
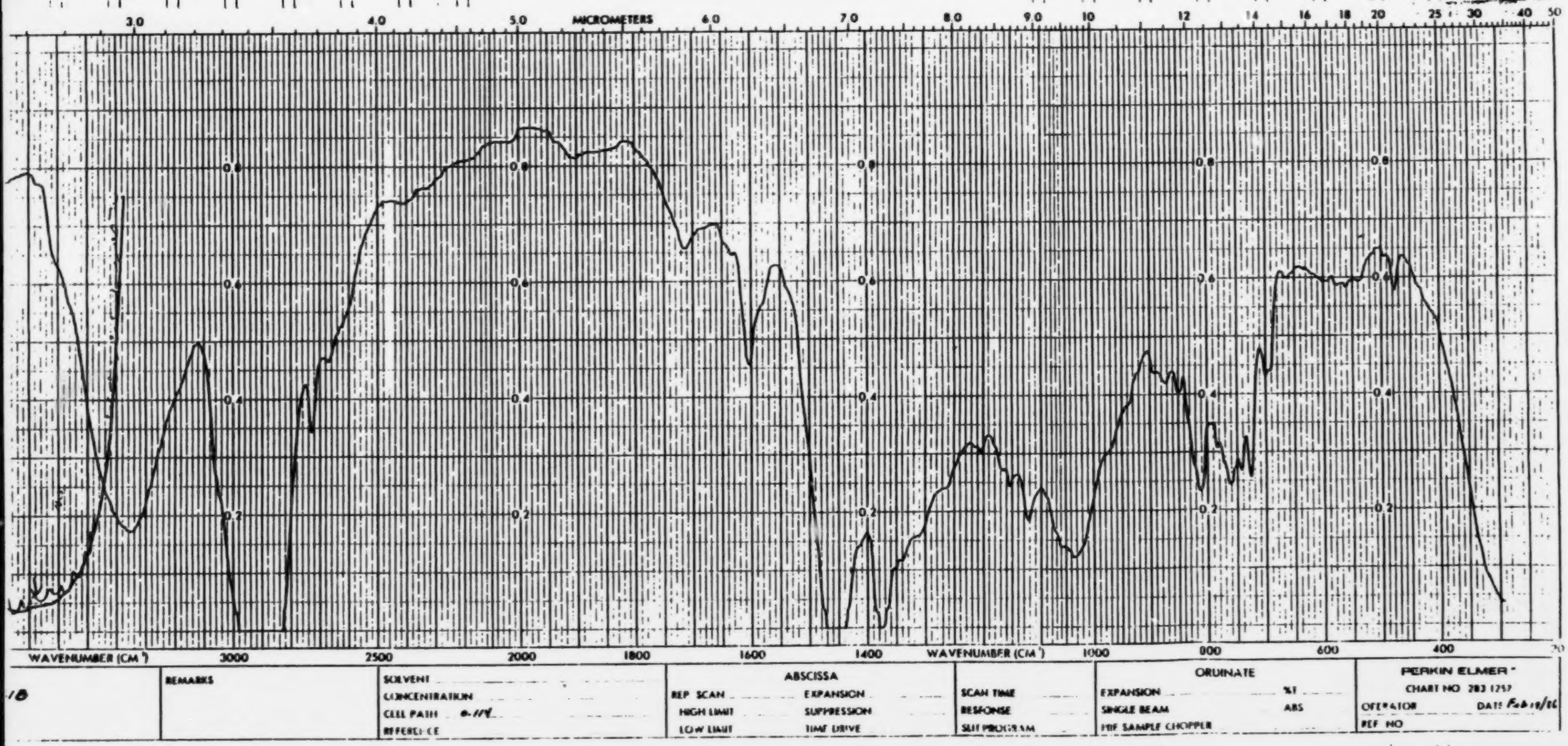


FIGURE 5.1E

SUNCOR COKER KEROSENE
API Sc
(SATURATE FRACTION)

FIGURE 5.1F

SUNCOR COKER KEROSENE
AP1 HB
(HYDROBORATED SAMPLE)



5.2 Suncor Hydrotreated Light Gas Oil

Combined Feed = AP2
Saturate Fraction = AP2 (SC)
Hydroborated Fraction = HB AP2

Suncor hydrotreated light gas oil (205°C-290°C) was a non-olefinic (0 wt.%) distillate containing 25 wt.% paraffin (3 wt.% n-paraffin), 50 wt.% cycloparaffin, 20 wt.% aromatics and 5 wt.% resin, (Table 5.2B). With the low aromatics content, the cetane index of the sample was 42, exceeding the minimum specification of 40. A summary of ASTM test results was summarized in Table 5.2A.

By low resolution mass spectrometry and gas chromatography mass spectrometry (Table 5.2B, 5.2C), the aromatics in the feed were mainly monoaromatics, and the saturates were mainly cycloparaffins.

Of the 26 wt.% paraffins, 12.2 wt.% were n-paraffins with the balance made up of iso-paraffins (Table 5.2D). Both LRMS and GCMS results were very similar in paraffin classification and the GCMS carbon number distribution matched the GC carbon number distribution (C_{11} to C_{18}).

Total ion current (TIC) traces and infrared scans were shown in Figures 5.2A to 5.2C and Figures 5.2D to 5.2F respectively. No olefins were detected by the GCMS and I.R. on hydroborated samples which is in good agreement with the bromine number of 0 wt.% olefins.

TABLE 5.2A

AP2 (COMBINED FEED)
SUNCOR HYDROTREATED LIGHT GAS OIL

Physical Characteristics

Density at 15°C g/cc		0.8381
Aniline Point, °C (ASTM D611)		59
Cetane Index (ASTM D976)		42
Cetane Index (CGSB)		43
Nitrogen Content, ppm		1
Sulfur Content, wt%		0
Carbon Content, wt%		86
Hydrogen Content, wt%		13
Oxygen Content, wt%		0
Viscosity @ 40°C, ASTM D445 (cSt)		2.2
Distillation, ASTM D86, Vol.%		
°C (GCD wt.%)	IBP	205
	10	215
	20	219
	30	223
	40	228
	50	232
	60	236
	70	241
	80	248
	90	258
	FBP	290
Average Molecular Weight (GCMS)		184
Average Molecular Weight (GCD)		183

TABLE 5.2B

AP2 (AS IS)
SUNCOR HYDROTREATED MIDDLE DISTILLATE

		Separation		
Components	LRMS	Fraction	Recal. LRMS	GCMS
Weight %				
Saturates	79	77	75	84
Paraffins	26	-	25	26
Cycloparaffins	53	-	50	58
Aromatics	21	20	20	16
Mono-Di	21	19	19	16
Polynuclear	0	1	1	0
Resins	0	3	5	0

TABLE 5.2C

MASS SPECTROMETRY COMPOSITIONAL DATA
SUNCOR HYDROGENATED LIGHT GAS OIL
FEED (AP2) AND SATURATES [AP2 (SC)]

		Feed		Saturates	
	Z Numbers	LRMS	GCMS	LRMS	GCMS
Saturates		79	84	99	99
Paraffins	+2	26	26	34	31
Cycloparaffins		53	58	65	68
Noncond. Cycloparaffins	0	25	29	30	34
Cond. Dicycloparaffins	-2	22	24	27	27
Cond. Polycycloparaffins	-4	6	5	8	7
Aromatics		21	16	1	1
Monoaromatics		19	15	1	1
Alkylbenzenes	-6	9	8	1	1
Benzocycloparaffins	-8	8	6	0	0
Benzodicycloparaffins	-10	2	1	0	0
Diaromatics		2	1	0	0
Naphthalenes	-12	1	1	0	0
Naphthocycloparaffins	-14	0	0	0	0
Fluorenes	-16	0	0	0	0
Triaromatics	-18,-20	0	0	0	0
Tetraaromatics	-22,-24	0	0	0	0
Pentaaromatics	-26,-28,-30	0	0	0	0
Unidentified	-32 to -44	0	0	0	0
Aromatic Sulfurs	-105,-165,-225	0	0	0	0

TABLE 5.2D

PARAFFIN CONTENT
SUNCOR HYDROTREATED LIGHT GAS OIL - AP2(SC)
MASS SPECTROMETRY AND GAS CHROMATOGRAPHY DATA

Components	Feed		Saturates	
	LRMS	GCMS	LRMS	GCMS
Saturates	100	100	100	100
Paraffins	33	31	34	31
Cycloparaffins	67	69	66	69
Noncond. Cycloparaffins	31	34	30	34
Cond. Dicycloparaffins	27	29	27	27
Cond. Polycycloparaffins	8	6	9	8

	GCMS Wt.%	GC Wt.%	GC Wt.%
Normal Paraffins	12.2	11.2	
Isoparaffins	10	N.D.	-
Isoparaffins + Cycloparaffins	-	-	88.6
(% Toluene)	-	0	-
Normal Paraffin Distribution Carbon Number			
C10	0.2		0.7
C11	0.9	1.0	4.2
C12	3.0	3.0	13.4
C13	3.4	3.1	24.2
C14	3.1	2.2	23.4
C15	1.2	1.2	14.8
C16	0.4	0.4	5.8
C17	0.1	0.2	1.7
C18	0.1	0.1	0.4

TABLE 5.2E

OLEFIN CONTENT
SUNCOR HYDROTREATED LGO HB AP2

	HB AP2
Average MW (GCMS)	184
IR Wt.% OH	0
GCMS: wt. % TMS Ether	0
Bromine Number: wt.% Olefin	0

87 wt.% recovery of hydroborated sample

FIGURE 5.2A

DS-55 CROSS SCAN REPORT, RUN: 3F1049
AP2 COMPOSITE SUNCOR HT DIST 261-85-65 860304
+ TIC

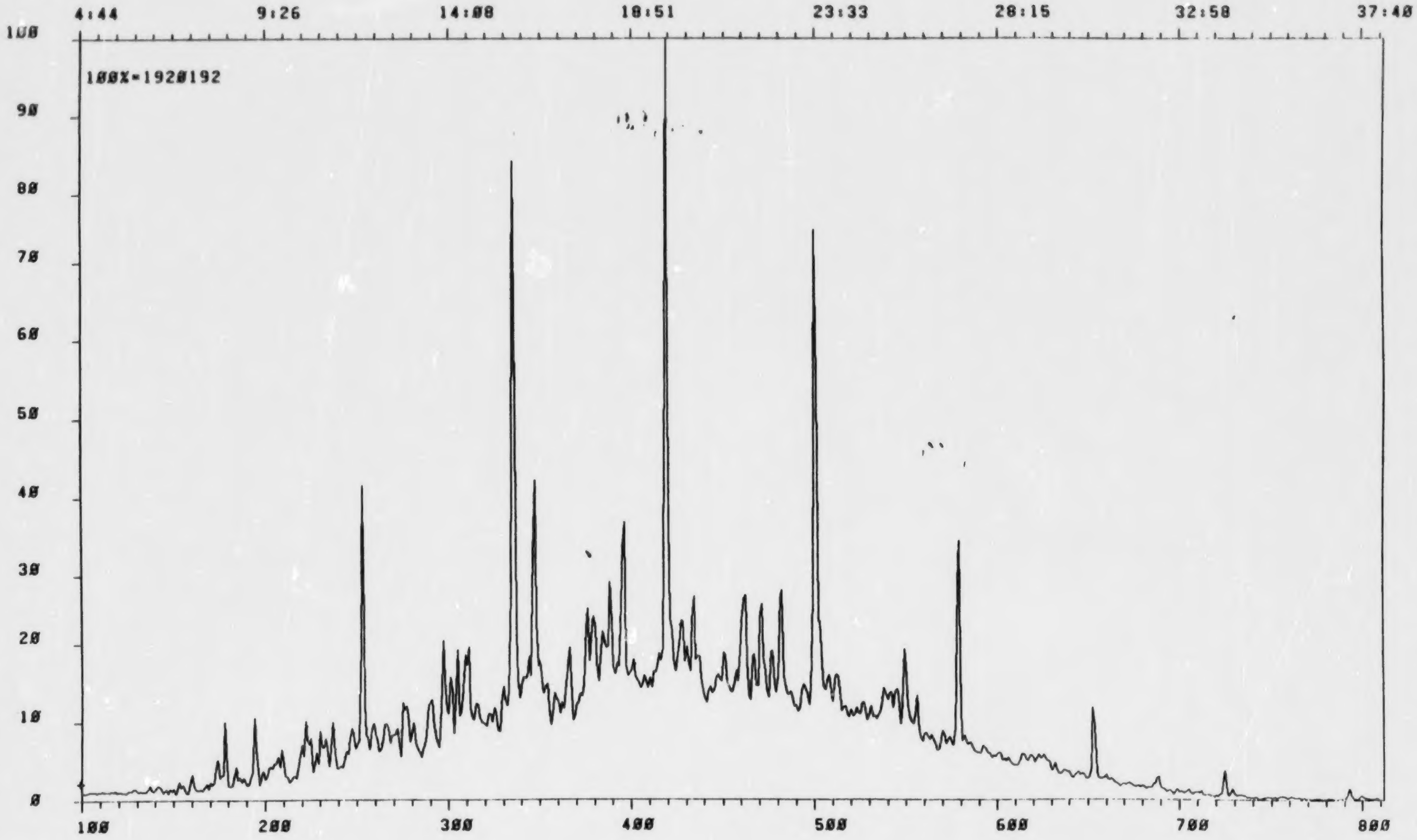


FIGURE 5.2B1

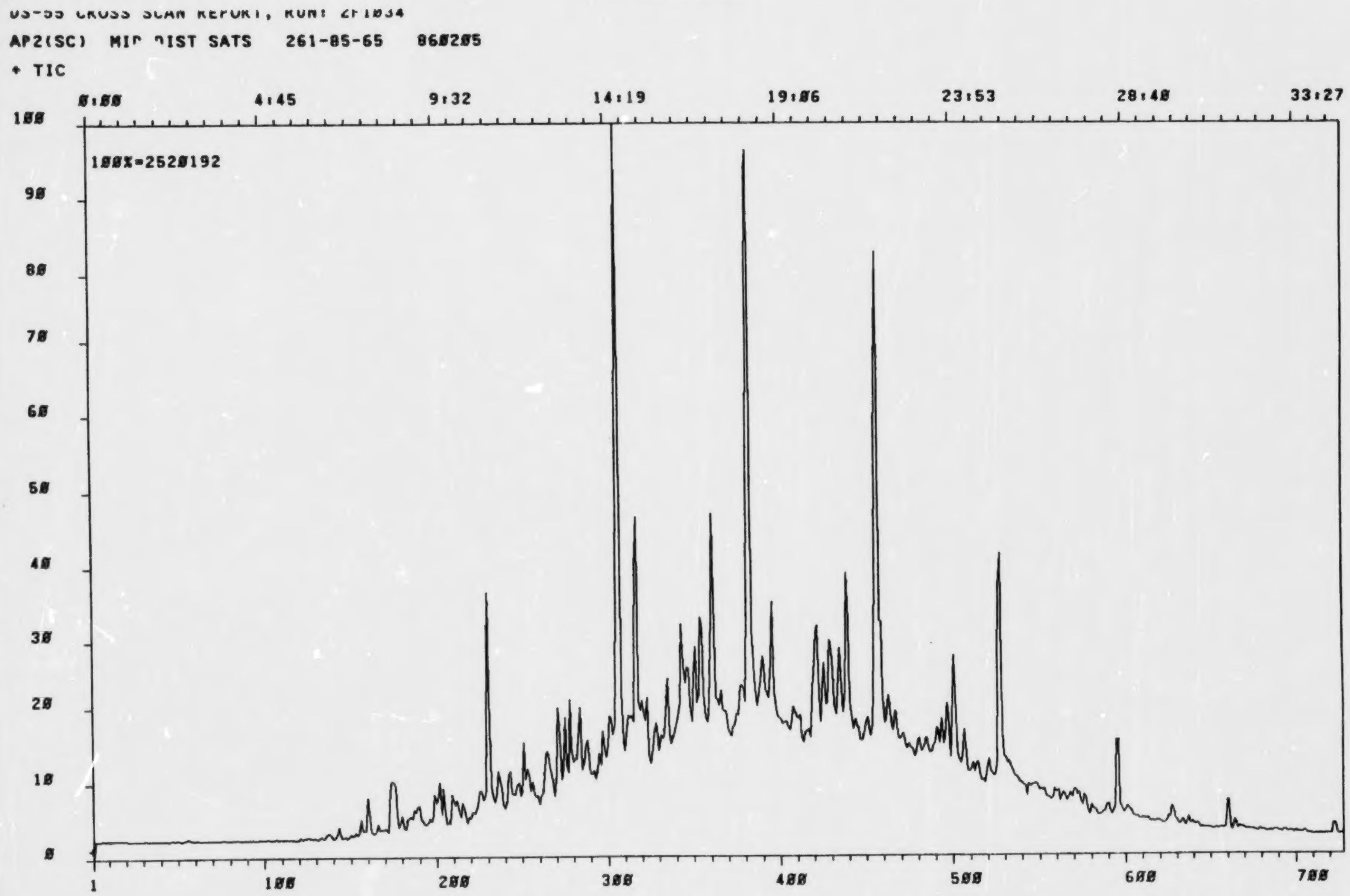
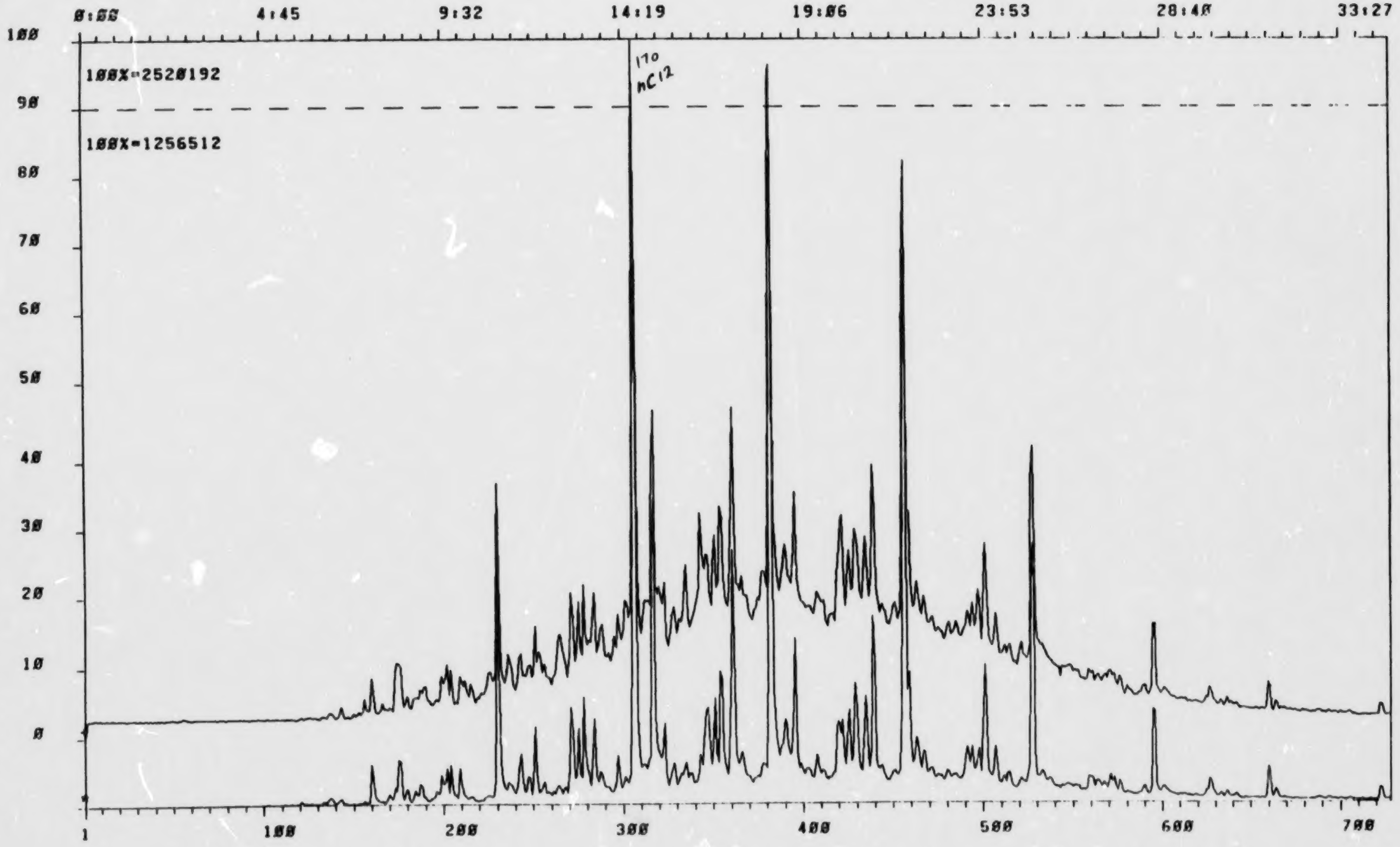

DS-55 CROSS SCAN REPORT, RUN: 2F1034
AP2(SC) MID DIST SATS 261-85-65 860205
+ TIC
100%=2520192
0:00
4:45
9:32
14:19
19:06
23:53
28:40
33:27
100
90
80
70
60
50
40
30
20
10
0
1
100
200
300
400
500
600
700

FIGURE 5.2B2

DS-55 CROSS SCAN REPORT, RUN: 2F1034
AP2(SC) M' 'IST SATS 261-85-65 860205
* 43 , 5/ , 71 , 85 , 99 + TIC



DS-55 CROSS SCAN REPORT, RUN: 3F1063
HB2B(1) SUNCOR HT DIST 261-85-65 860331
* 73 , 75 + TIC

FIGURE 5.2C

Graph 9

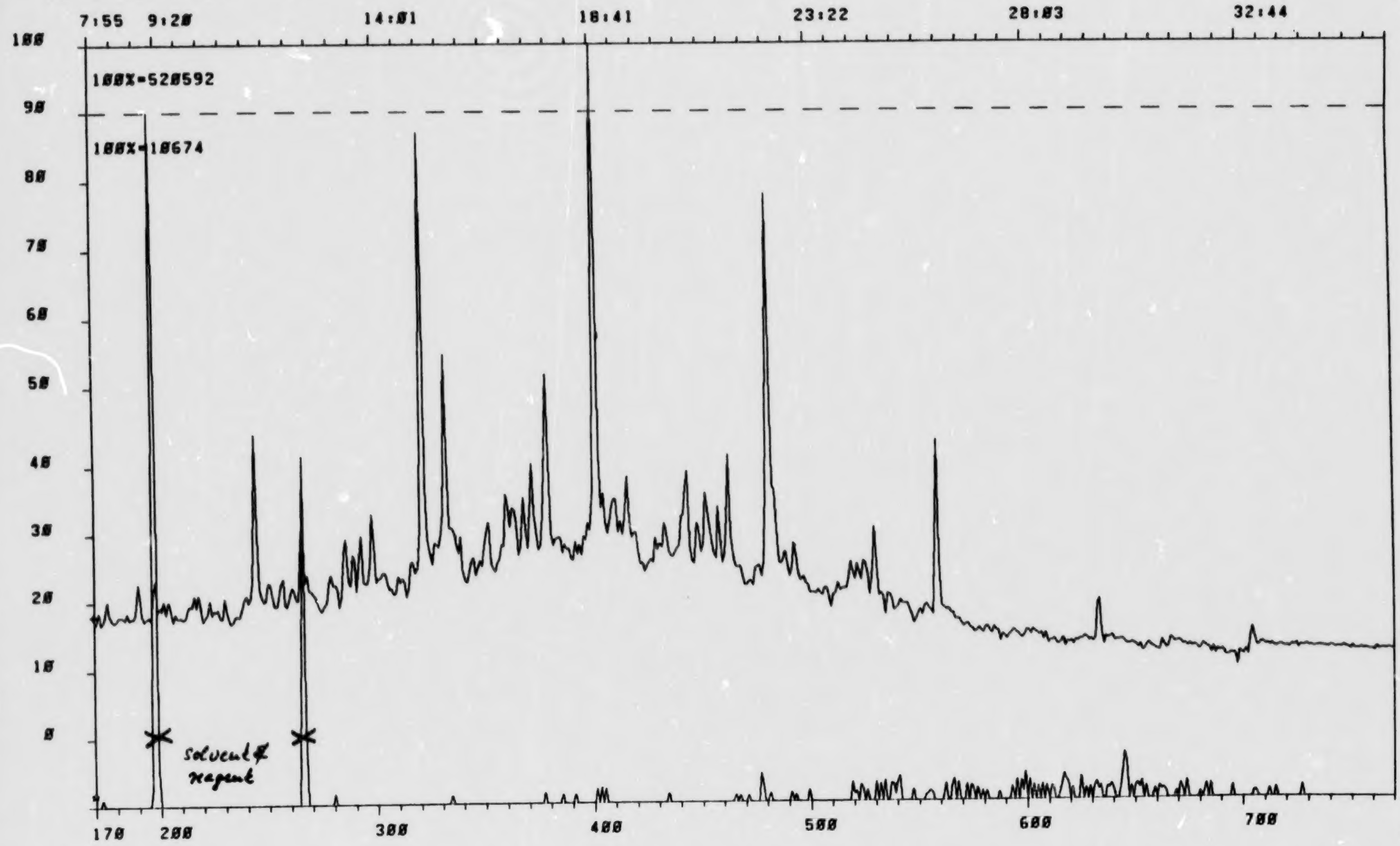
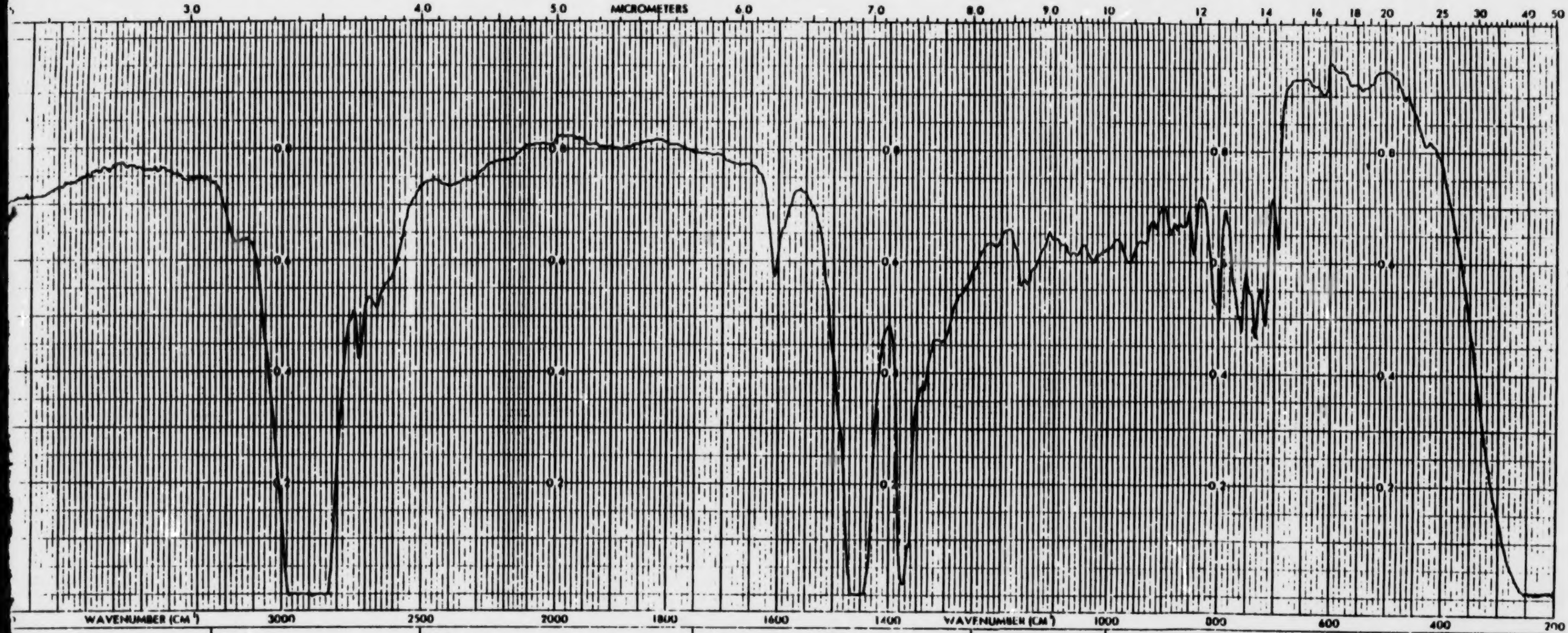


FIGURE 5.2D

SUNCOR HYDROTREATED LT. GAS OIL
AP2
(SAMPLE AS IS)



AMPLE AP2
Suncor Hydrotreat Light
Gas Oil
RIGIN

REMARKS

SOLVENT
CONCENTRATION
CELL PATH 0.081 mm
REFERENCE

ABSCISSA
REP SCAN
HIGH LIMIT
LOW LIMIT
EXPANSION
SUPPRESSION
TIME DRIVE

SCAN TIME 21
RESPONSE
SLIT PROGRAM

ORDINATE
EXPANSION
SINGLE BEAM
PRE SAMPLE CHOPPER
%T ✓
ABS

PERKIN ELMER®
CHART NO 283 1257
OPERATOR
DATE [illegible]
REF NO

FIGURE 5.2E

SUNCOR HYDROTREATED LT. GAS OIL

AP2 Sc

(SATURATE FRACTION)

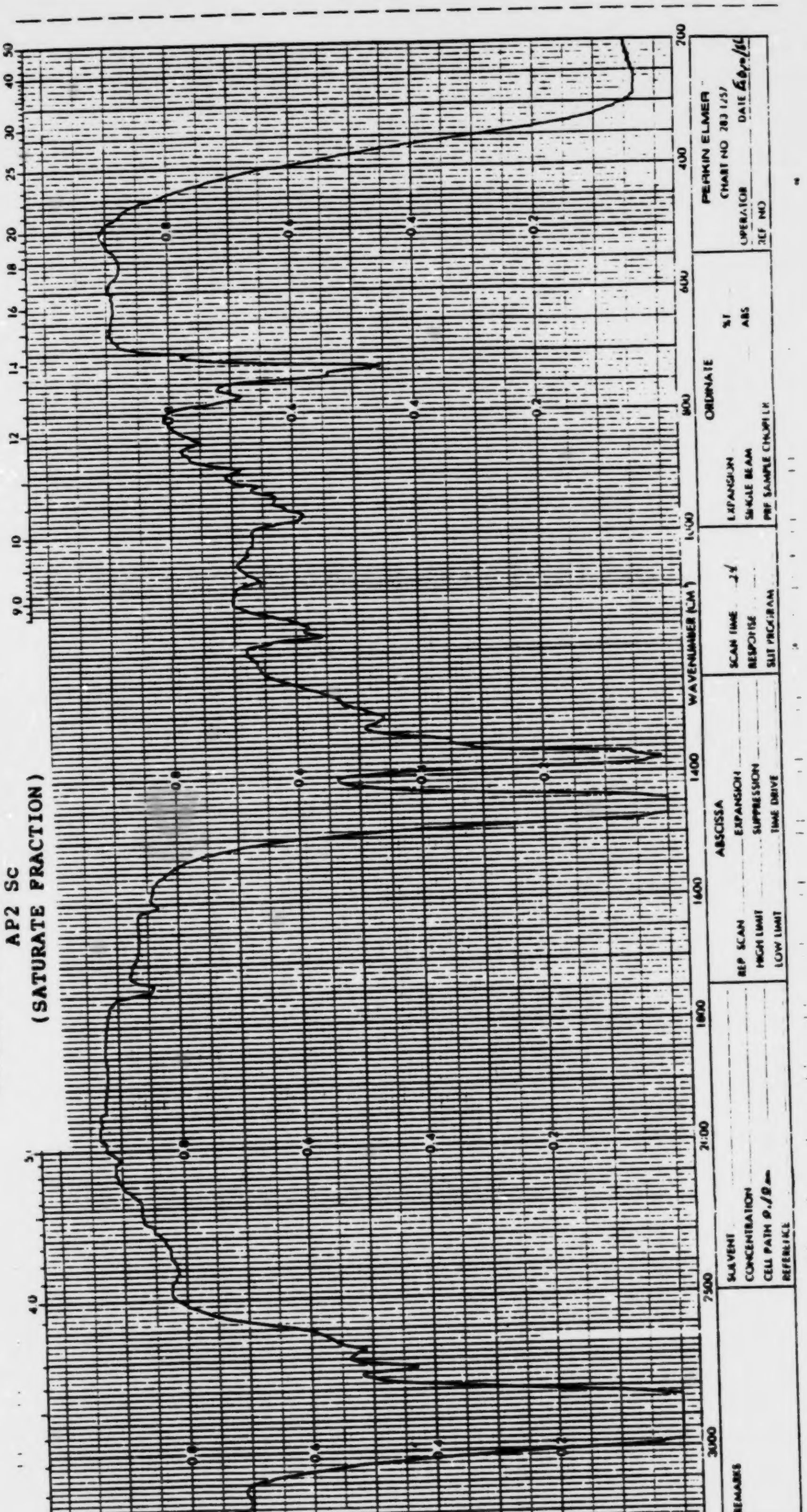
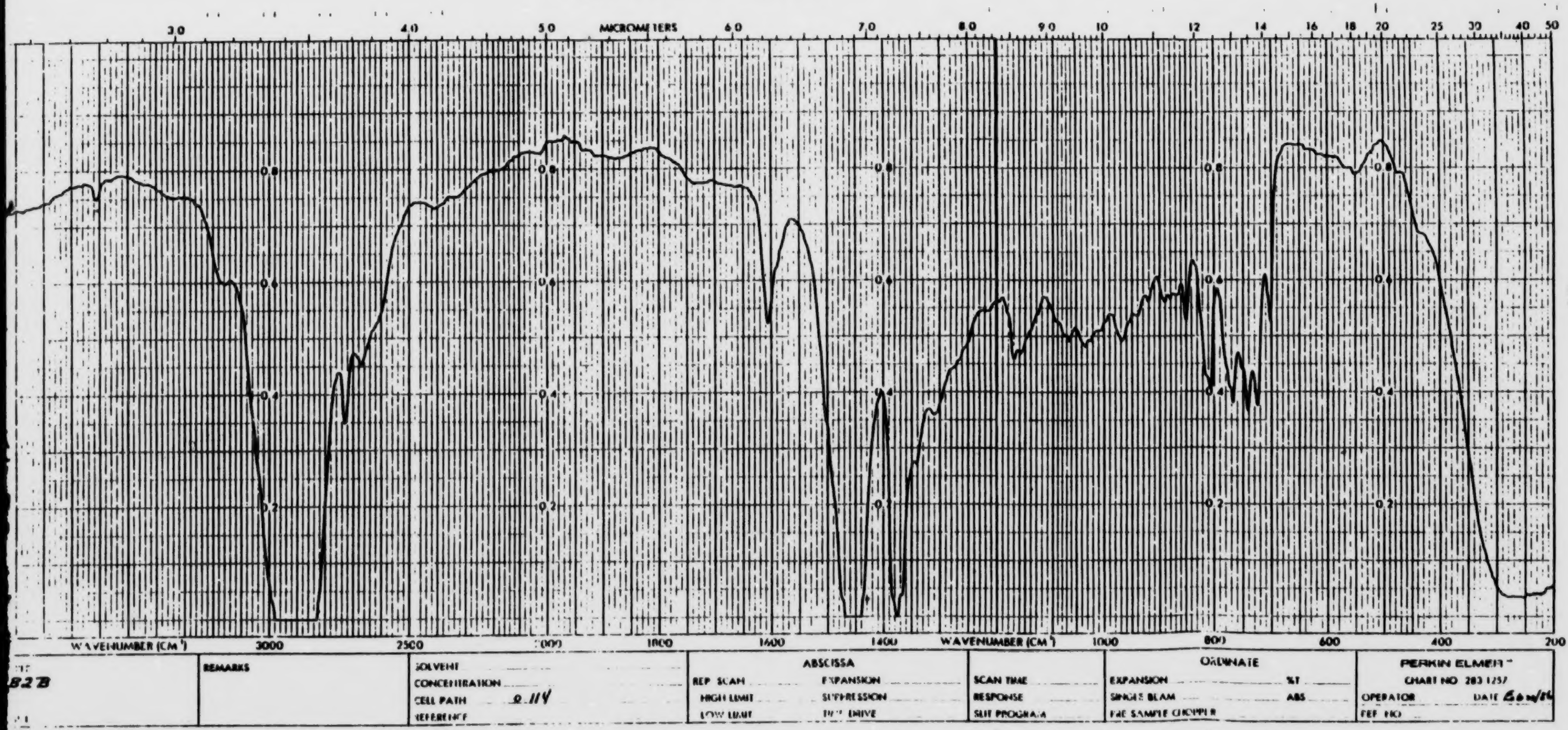


FIGURE 5.2F

SUNCOR HYDROTREATED LT. GAS OIL
AP1 HB
(HYDROBORATED SAMPLE)



5.3 Husky Fireflood

Combined Feed = AP3
Saturate Fraction = AP3 (SC)
Hydroborated Fraction = HB AP3

Husky fireflood material is a 207°C to 340°C nonolefinic distillate containing 12 wt.% paraffin (0.3 wt.% n-paraffin), 52 wt.% cycloparaffin, 31 wt.% aromatics and 5 wt.% resins (Table 5.3B).

The hydrocarbon composition by LRMS agreed well with the recalculated hydrocarbon separation by solvent elution but does not agree very well with GCMS feed results (Table 5.3B and 5.3C).

The paraffin content of the saturate fraction [AP3 (SC)] by both GCMS and GC (Table 5.3D) are in good agreement with carbon number distribution for n-paraffin fraction between C_{10} and C_{19}. The n-paraffin content of this distillate is very low (2.6 wt.% in saturate fraction) indicating that most of the paraffins are isoparaffinic and cycloparaffinic.

This highly branched distillate was confirmed by the GCMS molecular ion trace where few molecular ion trace features, except for 7-12 (alky-naphthalenes) could be detected. The lack of molecular ion features suggests that most substituents of the aromatic nucleus are highly branched much like the predominantly branched paraffin content of the sample.

No olefins were detected by GCMS (Figures 5.3A-5.3C) or I.R. (Figures 5.3D-5.3F) as illustrated in Table 5.3E. The reason for the high bromine number determination is not known.

TABLE 5.3A

AP3 (COMBINED FEED)
HUSKY FIREFLOOD

Physical Characteristics

Density at 15°C g/cc	0.8876
Aniline Point, °C (ASTM D611)	54.6
Cetane Index (ASTM D976)	41
Cetane Index (CGSB)	-
Nitrogen Content, ppm	20
Sulfur Content, wt%	1
Carbon Content, wt%	86
Hydrogen Content, wt%	13
Oxygen Content, wt%	0
Viscosity @ 40°C, ASTM D445 (cSt)	4.2
Distillation, ASTM D86, Vol.%	
°C (GCD wt.%) IBP	207
10	237
20	253
30	268
40	280
50	290
60	299
70	*
80	*
90	*
FBP	*
Average Molecular Weight (GCMS)	198
Average Molecular Weight (GCD)	237

* The sample foamed during D86

TABLE 5.3B

AP3 (AS IS)
HUSKY FIREFLOOD MIDDLE DISTILLATE (160-340°C)

Components	LRMS	Separation	Recal. LRMS	GCMS
Weight %				
Saturates	68	70	64	76
Paraffins	10	-	12	13
Cycloparaffins	58	-	52	63
Aromatics	32	25	31	24
Mono-Di	27	22	24	21
Polynuclear	5	3	7	3
Resins	0	5	5	0

TABLE 5.3C

MASS SPECTROMETRY COMPOSITIONAL DATA
HUSKY FIREFLOOD
FEED (AP3) AND SATURATES [AP3 (SC)]

	Z Numbers	Feed		Saturates	
		LRMS	GCMS	LRMS	GCMS
Saturates		68	76	92	92
Paraffins	+2	10	13	17	17
Cycloparaffins		58	63	75	75
Noncond. Cycloparaffins	0	24	28	30	34
Cond. Dicycloparaffins	-2	22	24	28	28
Cond. Polycycloparaffins	-4	12	11	17	13
Aromatics		32	24	8	8
Monoaromatics		18	16	5	7
Alkylbenzenes	-6	7	7	3	5
Benzocycloparaffins	-8	6	4	1	1
Benzodicycloparaffins	-10	5	5	1	1
Diaromatics		9	5	1	1
Naphthalenes	-12	4	3	0	0
Naphthocycloparaffins	-14	2	1	0	0
Fluorenes	-16	3	1	1	1
Triaromatics	-18,-20	2	1	1	0
Tetraaromatics	-22,-24	0	0	0	0
Pentaaromatics	-26,-28,-30	0	0	0	0
Unidentified	-32 to -44	0	0	0	0
Aromatic Sulfurs	-105,-165,-225	3	2	1	0

TABLE 5.3D

PARAFFIN CONTENT
HUSKY FIREFLOOD AP3(SC)
MASS SPECTROMETRY AND GAS CHROMATOGRAPHY DATA

Components	Feed		Saturates	
	LRMS	GCMS	LRMS	GCMS
Saturates	100	100	100	100
Paraffins	15	17	18	18
Cycloparaffins	85	83	81	81
Noncond. Cycloparaffins	35	37	33	37
Cond. Dicycloparaffins	33	32	30	30
Cond. Polycycloparaffins	17	14	18	14

	GCMS Wt.%	GC Wt.%	GC Wt.%
Normal Paraffins	2.6	1.7	-
Isoparaffins	4.3	N.D.	-
Isoparaffins + Cycloparaffins	-	-	98.3
(% Toluene)	-	0.4	-
Normal Paraffin Distribution Carbon Number			
C10	0.4	0.3	0.9
C11	0.2	0.1	2.8
C12	0.1	0.1	4.7
C13	0.4	0.1	8.1
C14	0.4	0.1	9.6
C15	0.4	0.4	9.4
C16	0.3	0.1	10.2
C17	0.2	0.1	10.5
C18	0.1	0.1	11.9
C19	0.1	0.2	10.1
C20	-	-	10.0
C21	-	0.1	6.6
C22	-	-	3.2
C23	-	-	0.3

TABLE 5.3E

OLEFIN CONTENT
HUSKY FIREFLOOD - HB AP3

	HB AP3
Average MW (GCMS)	198
IR Wt.% OH	0
GCMS: wt. % TMS Ether	0
Bromine Number: wt.% Olefin	11

95 wt.% recovery of hydroborated sample

FIGURE 5.3A

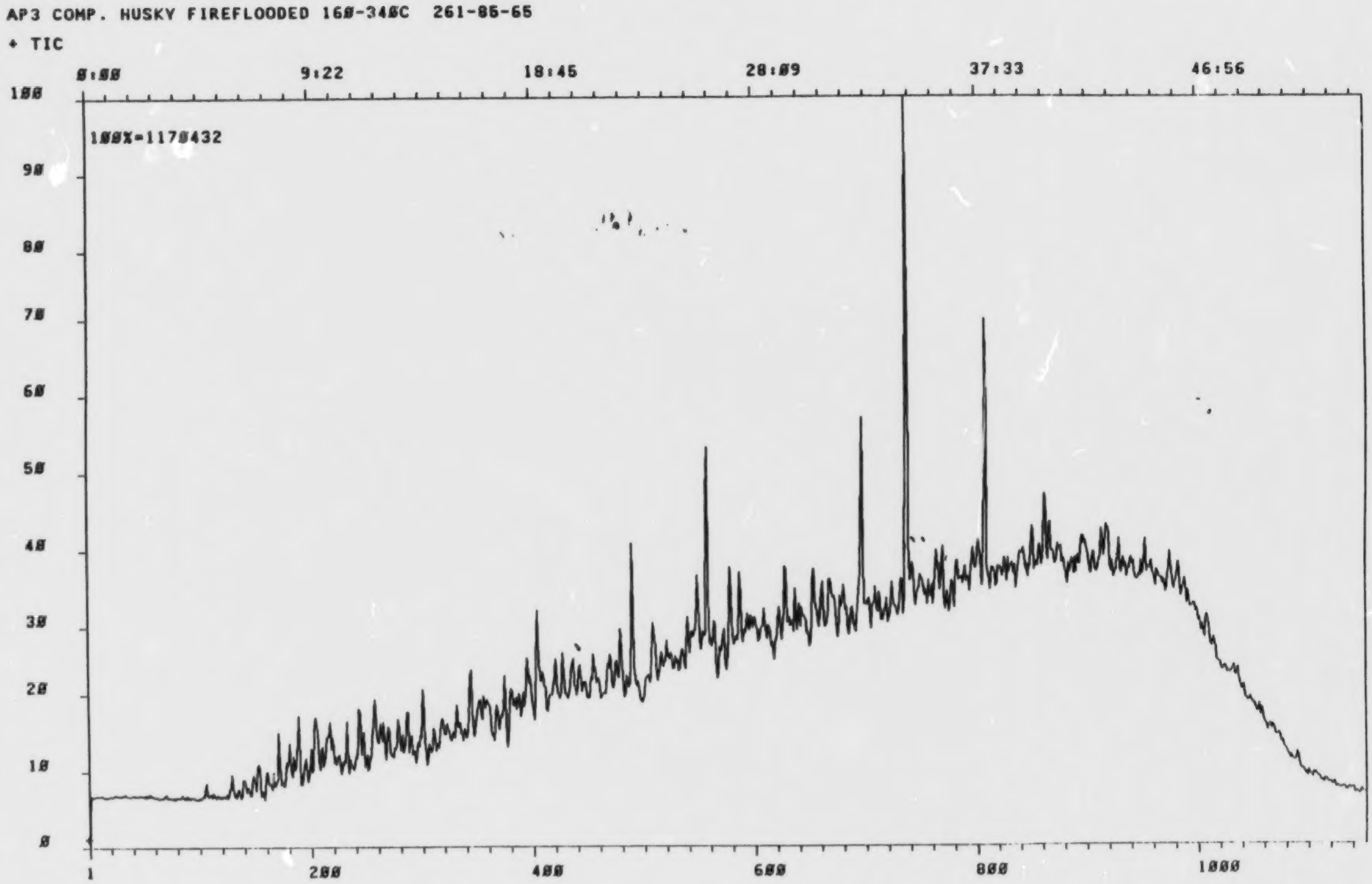

AP3 COMP. HUSKY FIREFLOODED 160-340C 261-85-65
+ TIC
0:00
9:22
18:45
28:09
37:33
46:56
100%=1170432
100
90
80
70
60
50
40
30
20
10
0
1
200
400
600
800
1000

FIGURE 5.3B

DS-55 CROSS SCAN REPORT, RUN: 2F1035
AP3(SC) MII ST SATS 261-85-65 860.
+ TIC

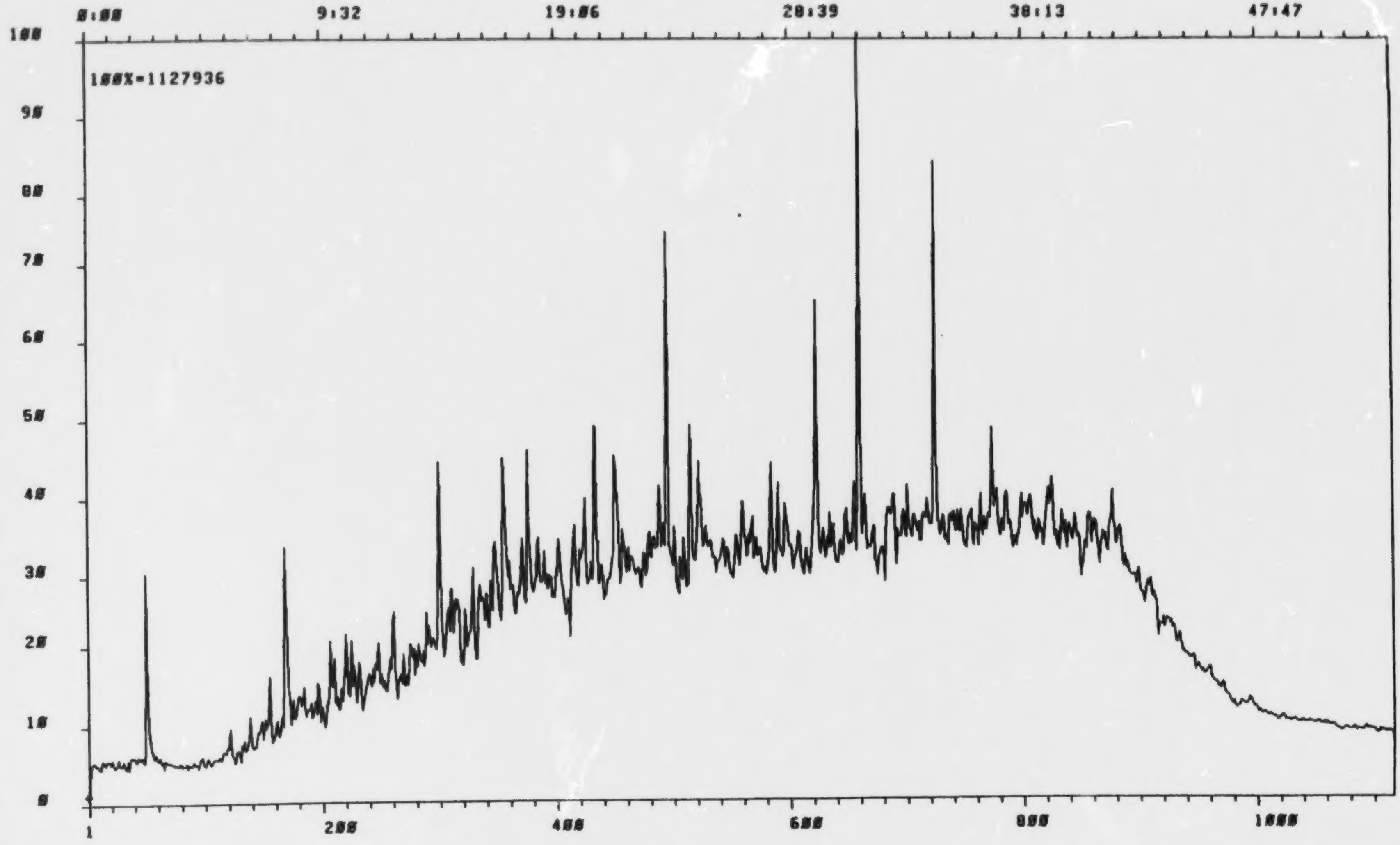


FIGURE 5.3C

Graph 10

DS-55 CROSS SCAN REPORT, RUN: 3F1062
HB3A(1) HUSKY FIREFLOODED 261-85-65 860331
* 73 , 75 + TIC

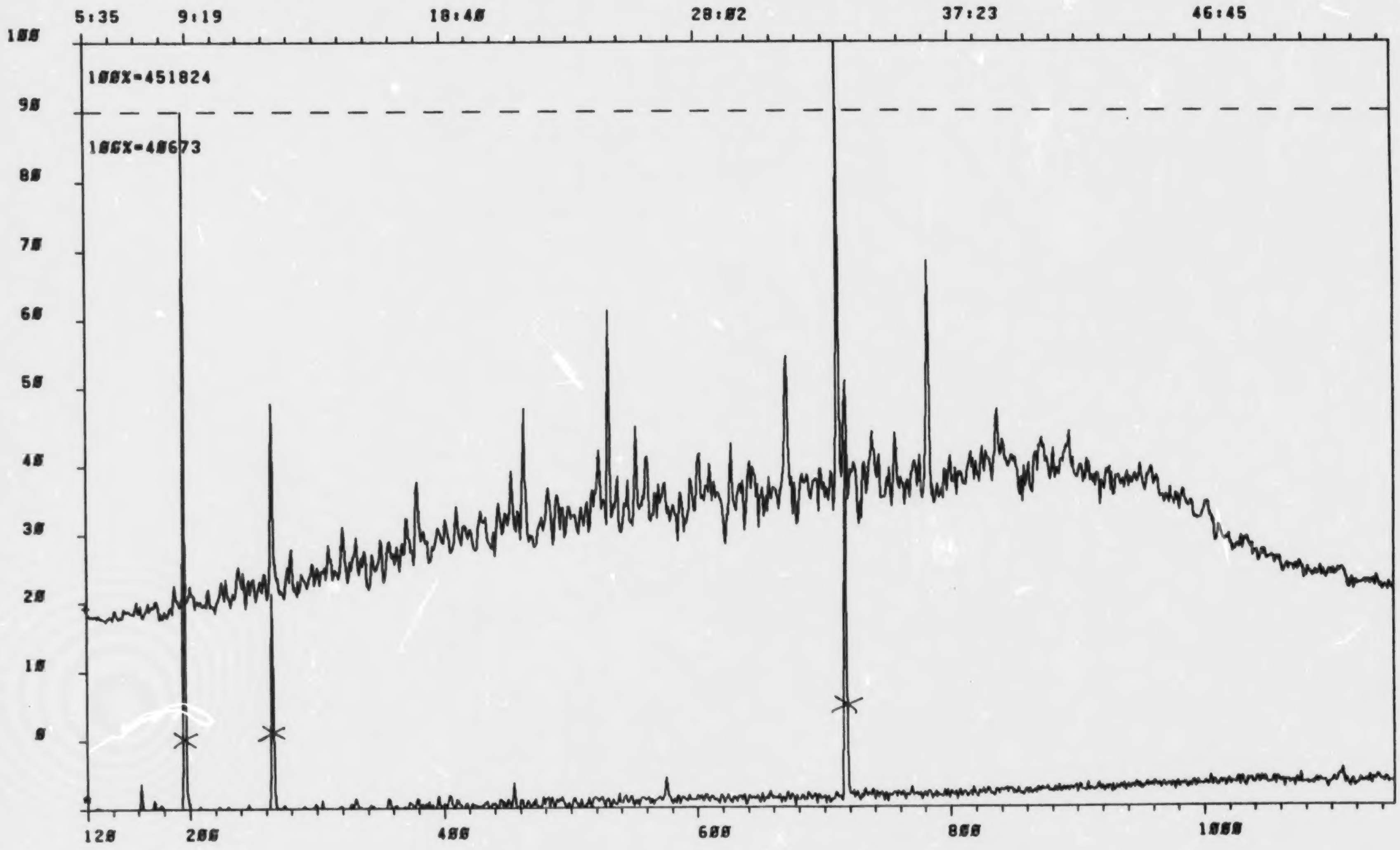
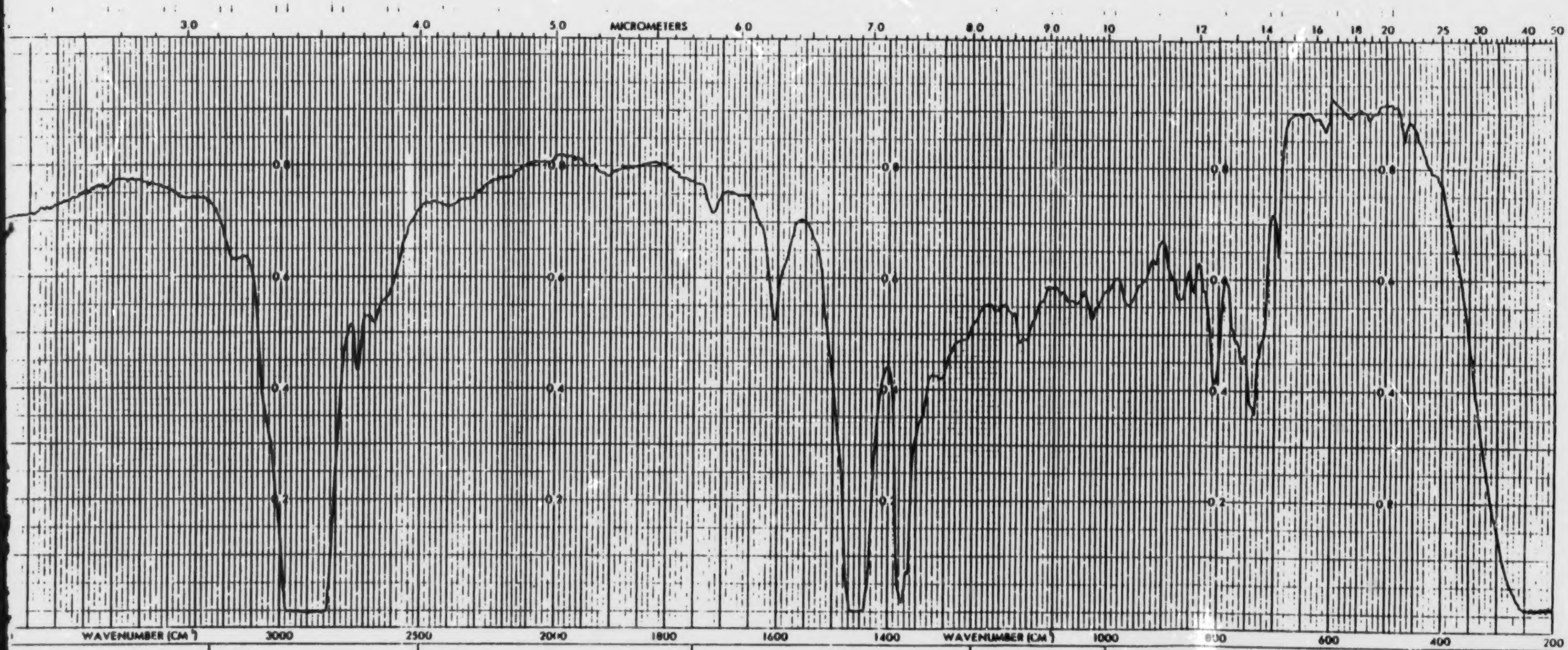


FIGURE 5.3D

HUSKY FIREFLOOD
AP3
(SAMPLE AS IS)



SAMPLE AP3
Husky Fire flood
ORIGIN 160°C - 340°C

REMARKS

SOLVENT
CONCENTRATION
CELL PATH .0081
REFERENCE

ABSCISSA
REP SCAN
HIGH LIMIT
LOW LIMIT
EXPANSION
SUPPRESSION
TIME DRIVE

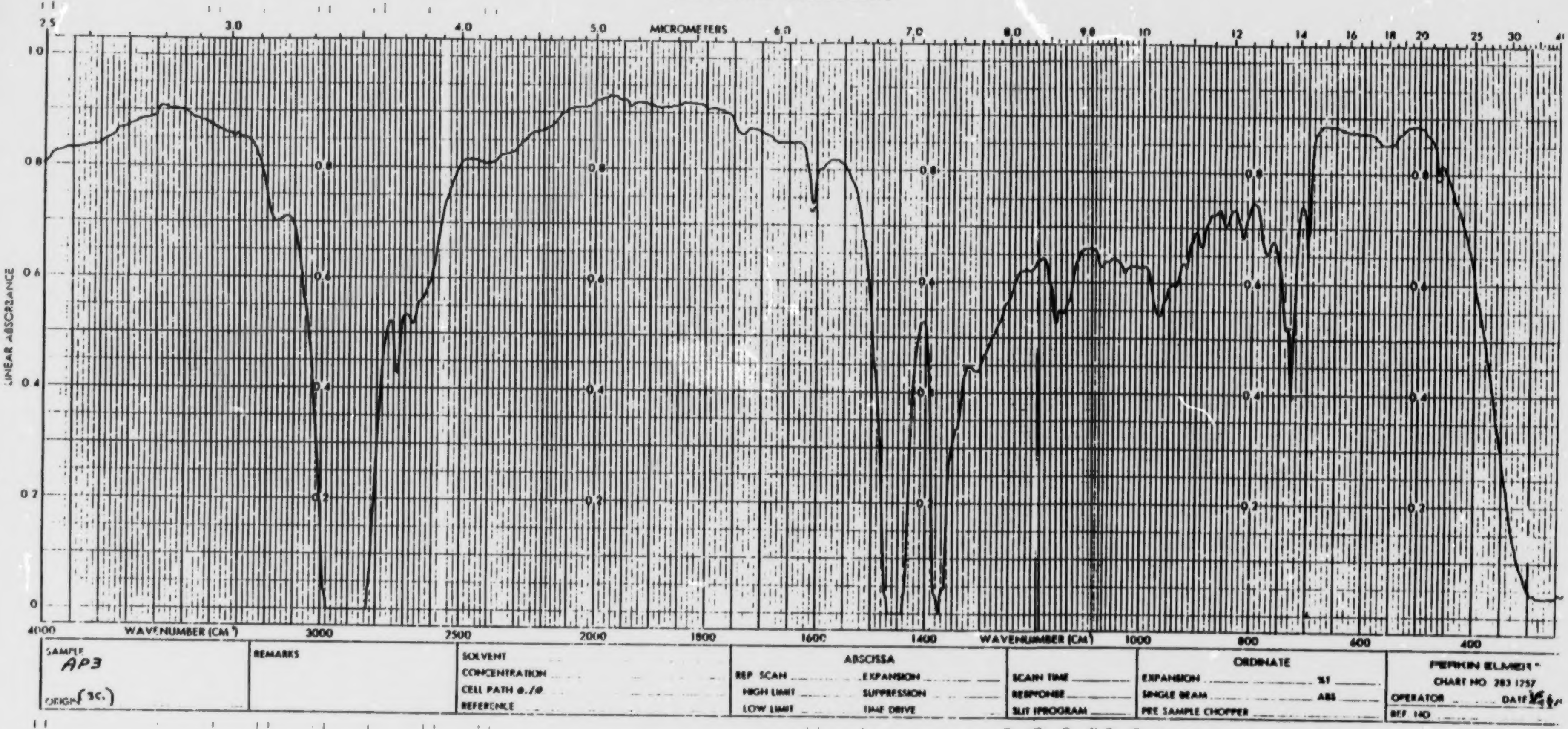
SCAN TIME
RESPONSE
SLIT PROGRAM

ORDINATE
EXPANSION
%T ✓
SINGLE BEAM
ABS
PRE SAMPLE CHOPPER

PERKIN ELMER ®
CHART NO 283 1257
OPERATOR
DATE July 15/85
REF NO

FIGURE 5.3E

HUSKY REFLOOD
AP3 SC
(SATURATE FRACTION)



SAMPLE AP3

ORIGIN (SC.)

REMARKS

SOLVENT

CONCENTRATION

CELL PATH 0.10

REFERENCE

REP SCAN

HIGH LIMIT

LOW LIMIT

EXPANSION

SUPPRESSION

TIME DRIVE

SCAN TIME

RESPONSE

SLIT PROGRAM

EXPANSION %T

SINGLE BEAM ABS

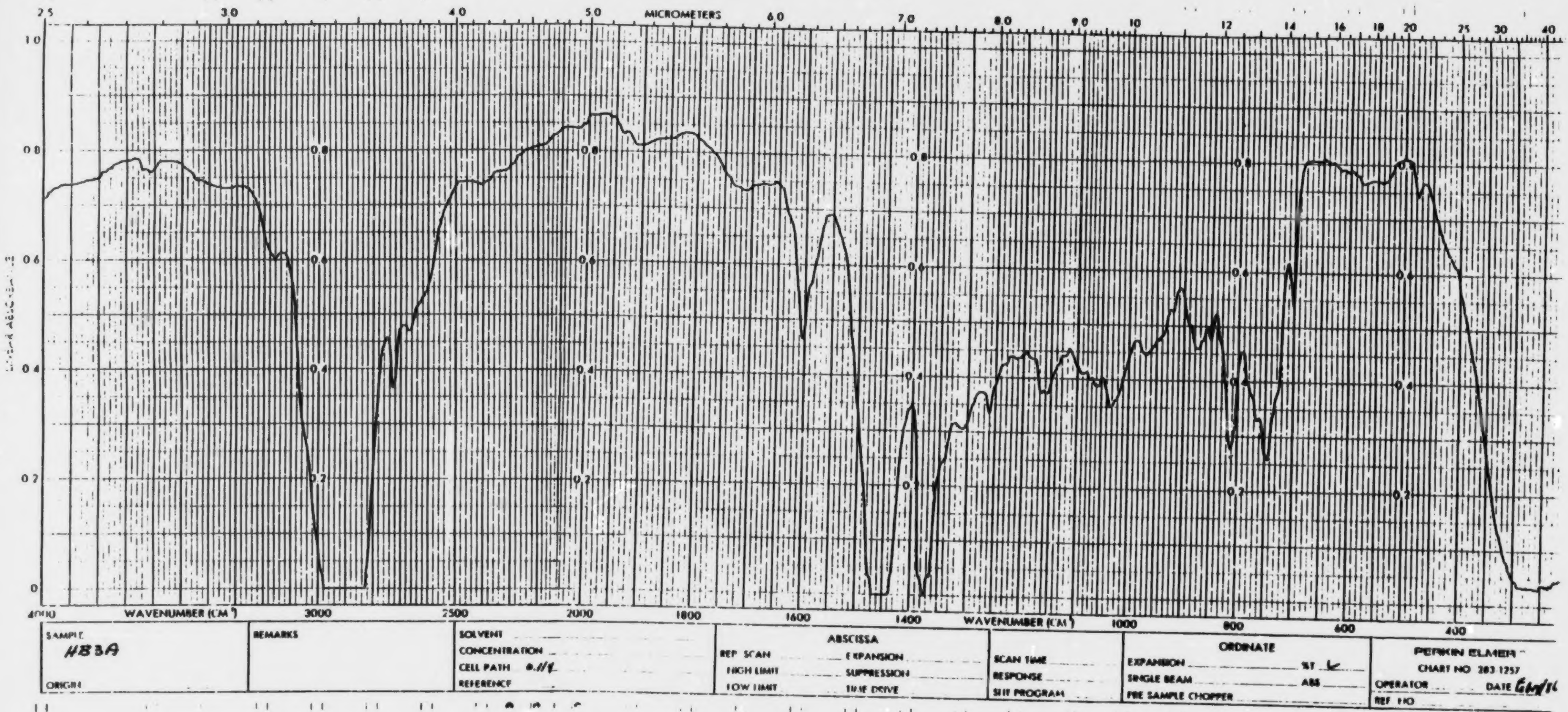
PRE SAMPLE CHOPPER

OPERATOR

DATE

REF NO

FIGURE 5.3F
HUSKY EFLOOD
AP3 HB
(HYDROBORATED SAMPLE)



5.4 Wyodak Liquified Coal

Combined Feed = AP4
Saturate Fraction = AP4 (SC)
Hydroborated Fraction = HB AP4

The Wyodak liquified coal distillate contained phenolic compounds (6-8 wt.% by GCMS) which were detected by both GCMS and I.R. (Figures 5.4A to 5.4F). The two methods (Table 5.4B and 5.4C) LRMS and GCMS, used to determine hydrocarbon composition were in agreement with each other but did not agree with the hydrocarbon separation (solvent elution) procedure. The hydrocarbons identified as resins by one method were classified as cycloparaffins by LRMS and GCMS. The lack of molecular ion features (except 2-12 alkylnaphthelenes) suggests that most substituents of the aromatic nucleus are highly branched.

The saturate fraction of the sample (62 wt.%) was mainly cycloparaffins (59 wt.%) with a small amount (3 wt.%) of other paraffins. Although very small, n-paraffins analysed by GCMS agreed with the GC method (Table 5.4D). The cyclic nature of the sample had deleterious effect on cetane index (19) and hence diesel engine performance.

The infrared alcohol (Table 5.4E) content increased from 5.6 wt.% (phenols) on sample before hydroboration to 20 wt.% after hydroboration. The total olefin content was therefore 14 wt.% which agreed with the 13 wt.% olefins calculated from the bromine number and 14 wt.% by GCMS. The GCMS, Figure 5.4C1 (HBAP4) showed the TIC envelope and E73 and 75 ion plot reflecting the higher boiling point (increased molecular weight) by the TMS ether compared to the original sample. Figure 5.4C2 showed molecular ion plots for the TMS ether homologue of m/e 180-236 which originate from m/e 108-164 alkyl phenols.

TABLE 5.4A

AP4 (COMBINED FEED)
WYODAK LIQUIFIED COAL

Physical Characteristics

Density at 15°C g/cc	0.8734
Aniline Point, °C (ASTM D611)	28.5
Cetane Index (ASTM D976)	19
Cetane Index (CGSB)	27
Nitrogen Content, ppm	3000
Sulfur Content, wt%	0
Carbon Content, wt%	86
Hydrogen Content, wt%	13
Oxygen Content, wt%	1
Viscosity @ 40°C, ASTM D445 (cSt)	1.7
Distillation, ASTM D86, Vol.%	
°C (GCD wt.%) IBP	176
10	180
20	189
30	191
40	195
50	200
60	208
70	214
80	221
90	235
FBP	257
Average Molecular Weight (GCMS)	162
Average Molecular Weight (GCD)	167

TABLE 5.4B

AP4 (AS IS)
WYODAK LIQUIFIED COAL (160°C+) MIDDLE DISTILLATE

Components	LRMS	Separation Fractions	Separation Recal. LRMS	GCMS
Weight %				
Saturates	78	67	62	81
Paraffins	2	-	3	2
Cycloparaffins	76	-	59	79
Aromatics	22	19	24	19
Mono-Di	22	18	23	19
Polynuclear	0	1	1	0
Resins	0	14	14	0

TABLE 5.4C

MASS SPECTROMETRY COMPOSITIONAL DATA
WYODAK LIQUIFIED COAL
FEED (AP4) AND SATURATES [AP4 (SC)]

		Feed		Saturates	
	Z Numbers	LRMS	GCMS	LRMS	GCMS
Saturates		78	81	93	100
Paraffins	+2	2	2	5	4
Cycloparaffins		76	79	88	96
Noncond. Cycloparaffins	0	34	39	39	45
Cond. Dicycloparaffins	-2	35	32	45	47
Cond. Polycycloparaffins	-4	7	8	4	4
Aromatics		22	19	7	0
Monoaromatics		20	17	7	0
Alkylbenzenes	-6	7	6	7	0
Benzocycloparaffins	-8	12	10	0	0
Benzodicycloparaffins	-10	1	1	0	0
Diaromatics		2	2	0	0
Naphthalenes	-12	2	2	0	0
Naphthocycloparaffins	-14	0	0	0	0
Fluorenes	-16	0	0	0	0
Triaromatics	-18,-20	0	0	0	0
Tetraaromatics	-22,-24	0	0	0	0
Pentaaromatics	-26,-28,-30	0	0	0	0
Unidentified	-32 to -44	0	0	0	0
Aromatic Sulfurs	-105,-165,-225	0	0	0	0

TABLE 5.4D

PARAFFIN CONTENT
WYODAK LIQUIFIED COAL - AP4(SC)
MASS SPECTROMETRY AND GAS CHROMATOGRAPHY DATA

Components	Feed		Saturates	
	LRMS	GCMS	LRMS	GCMS
Saturates	100	100	100	100
Paraffins	3	2	5	4
Cycloparaffins	97	98	95	96
Noncond. Cycloparaffins	43	48	42	45
Cond. Dicycloparaffins	45	40	49	47
Cond. Polycycloparaffins	9	10	4	4

	GCMS Wt.%	GC Wt.%	GC Wt.%
Normal Paraffins	3.4	4.3	-
Isoparaffins	2.6	-	-
Isoparaffins + Cycloparaffins	-	-	95.7
(% Toluene)	-	7.1	-
Normal Paraffin Distribution Carbon Number			
C 9	0.2	0.0	0.8
C10	0.4	0.3	20.6
C11	0.5	1.2	23.7
C12	1.0	0.9	21.9
C13	0.6	0.7	13.8
C14	0.3	0.8	10.2
C15	0.3	0.2	4.0
C16	0.2	0.2	0.7
C17	0.2	0.0	0.0

TABLE 5.4E

OLEFIN CONTENT
WYODAK LIQUIFIED COAL - HB AP4

	HB AP4
Average MW (GCMS)	162
IR Wt.% OH	14 (6)
GCMS: wt. % TMS Ether	14 (6)
Bromine Number: wt.% Olefin	13

( ) concentration on composite sample

95 wt.% recovery of hydroborated sample

FIGURE 5.4A

A

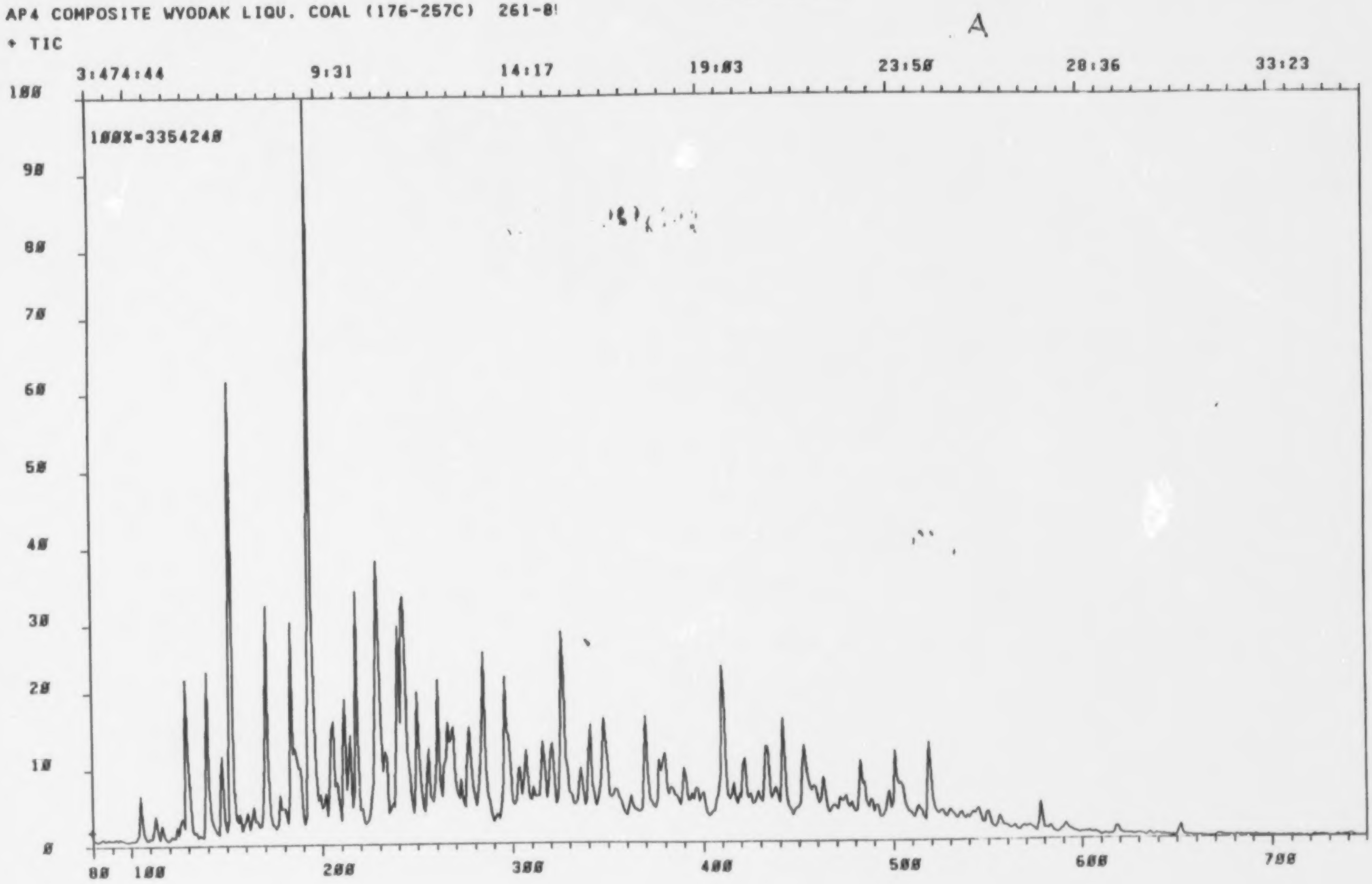
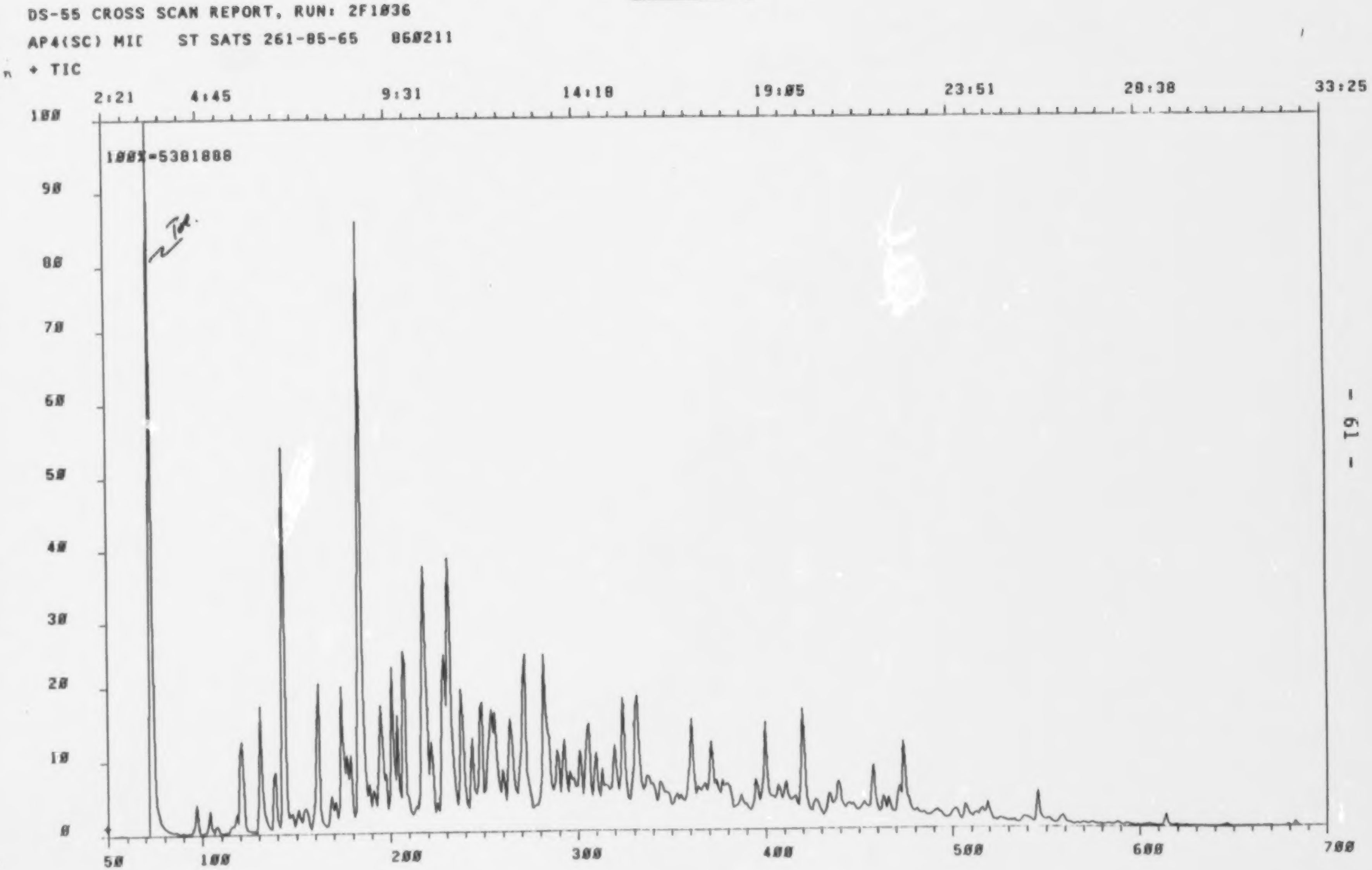

AP4 COMPOSITE WYODAK LIQU. COAL (176-257C) 261-8!
+ TIC
100X=3354240
3:474:44
9:31
14:17
19:03
23:50
28:36
33:23
100
90
80
70
60
50
40
30
20
10
0
80
100
200
300
400
500
600
700

FIGURE 5.4B


DS-55 CROSS SCAN REPORT, RUN: 2F1036
AP4(SC) MIC ST SATS 261-05-65 060211
+ TIC
2:21
4:45
9:31
14:18
19:05
23:51
28:38
33:25
100% =5301888
Tol.
100
90
80
70
60
50
40
30
20
10
0
50
100
200
300
400
500
600
700

DS-55 CROSS SCAN REPORT, RUN: 3F1060
HB4B(1) WYODAK LIQ COAL 261-85-65 860327
* 73 , 75 + TIC

FIGURE 5.4C1

Graph 3

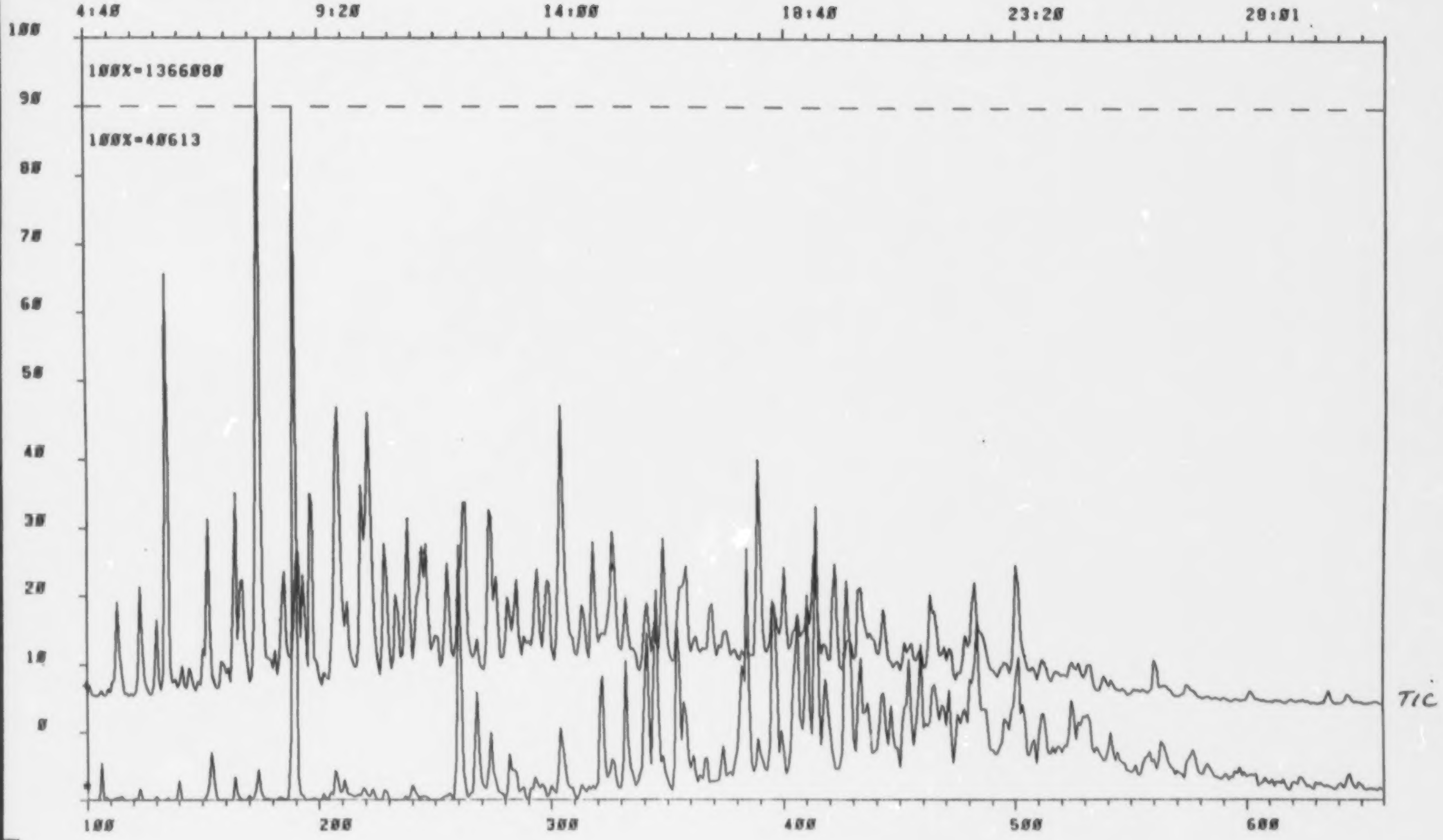


FIGURE 5.4C2

Graph 4

HB4B(1) WYODAK LIQ COAL 261-85-65 860327
* 236 # 222 O 208 & 194 $ 108 + TIC

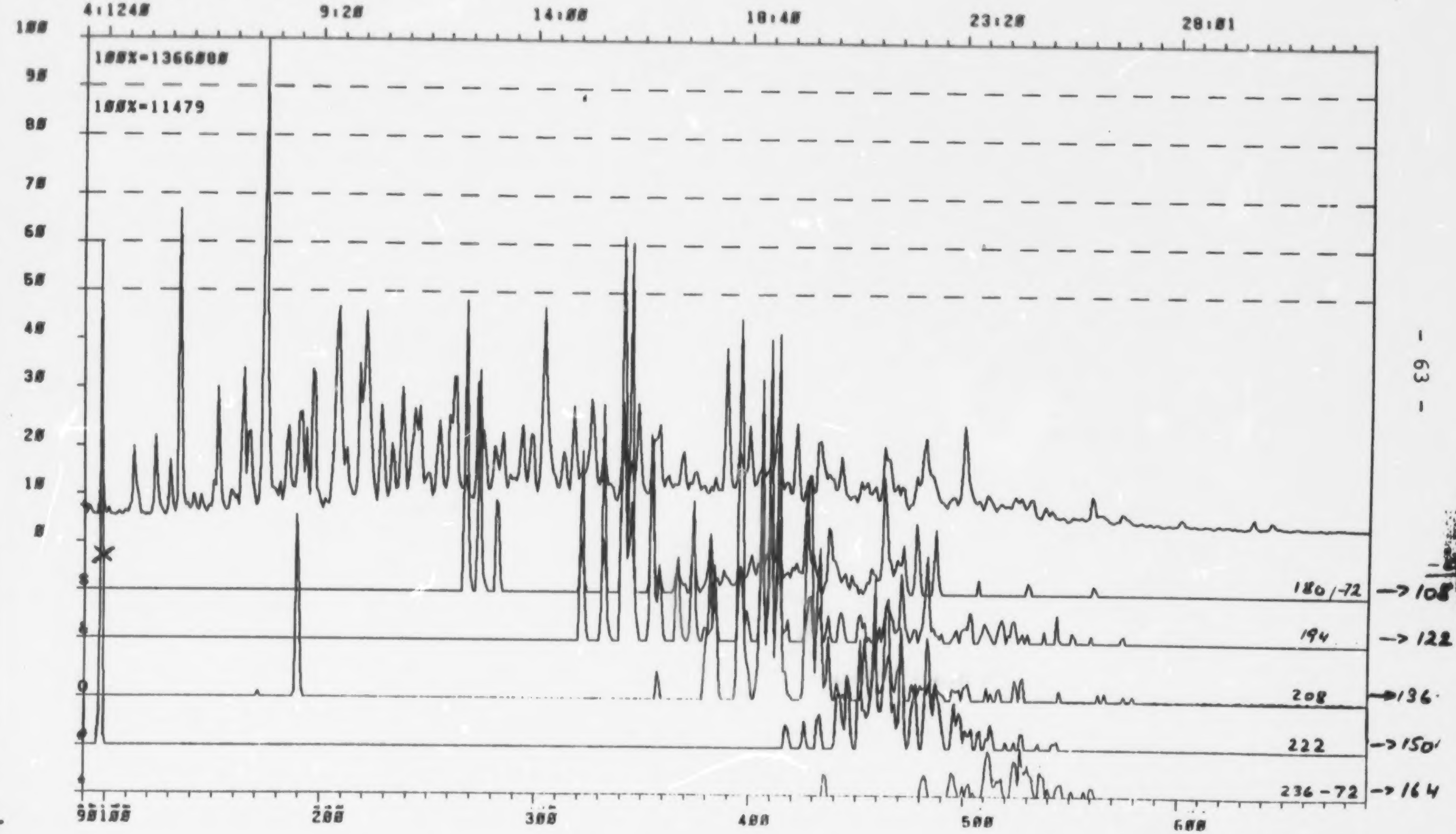


FIGURE 5.4D

WYODAK UIFIED COAL
AP4
(SAMPLE AS IS)

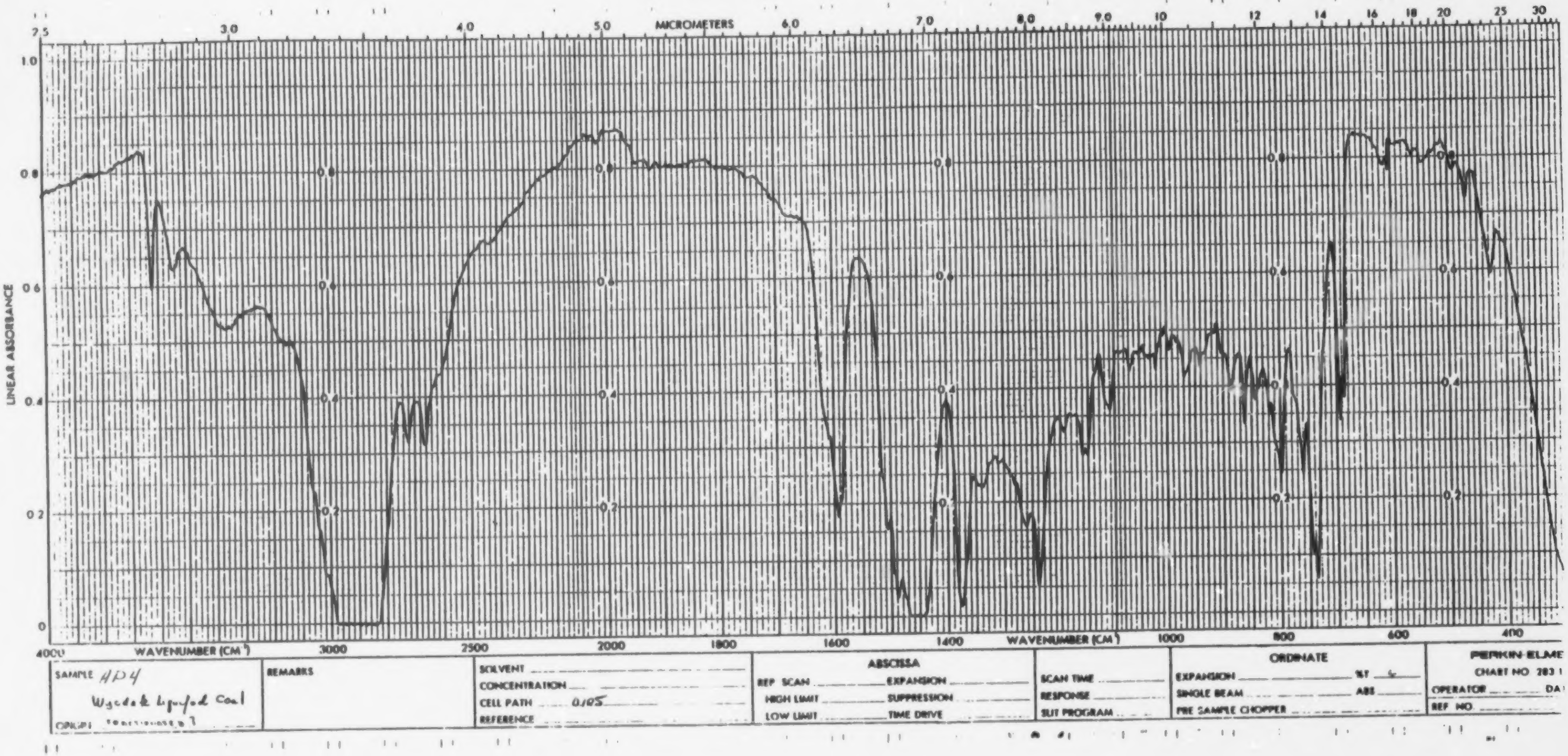


FIGURE 5.4E

WYODAK LIQUIFIED COAL
AP4 Sc
(SATURATE FRACTION)

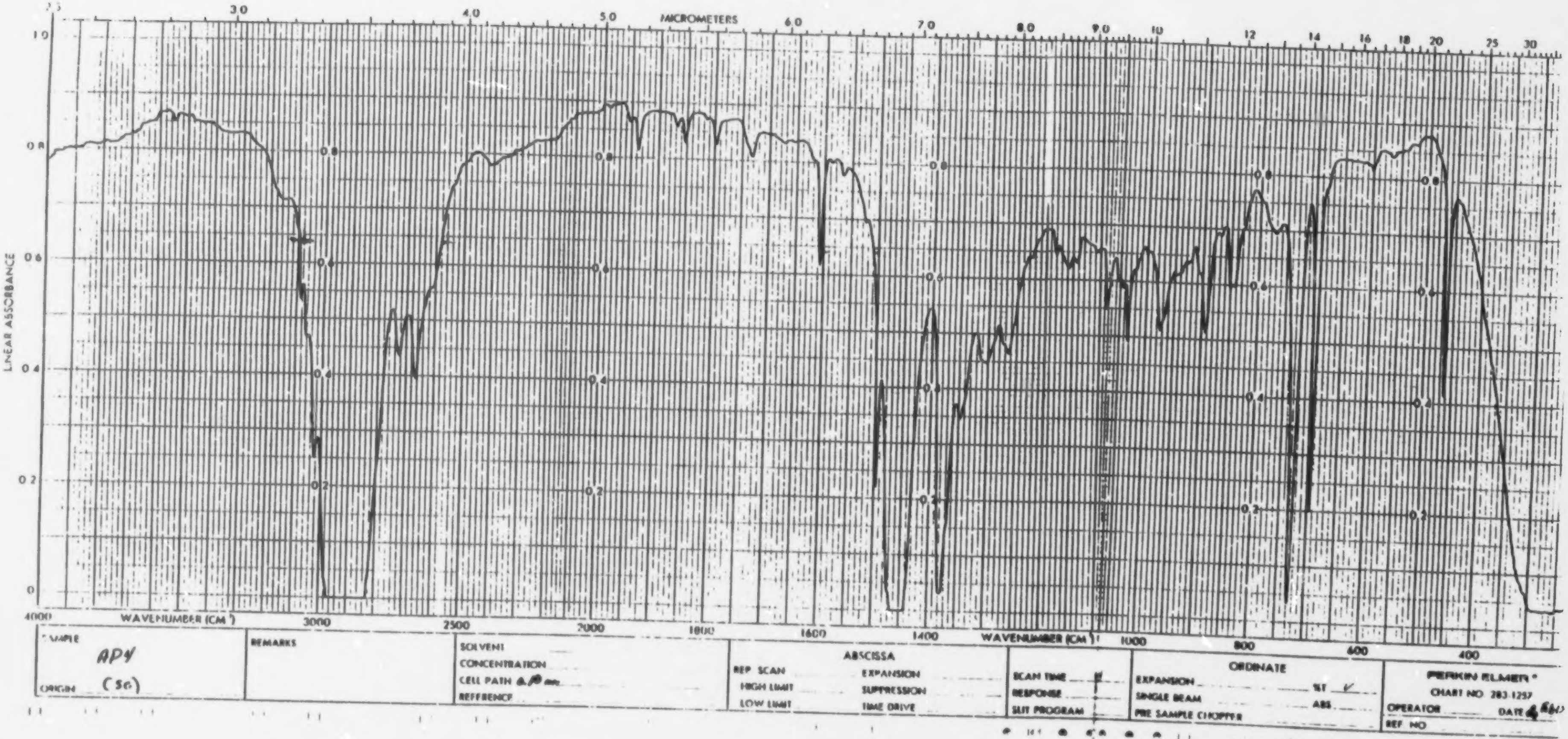
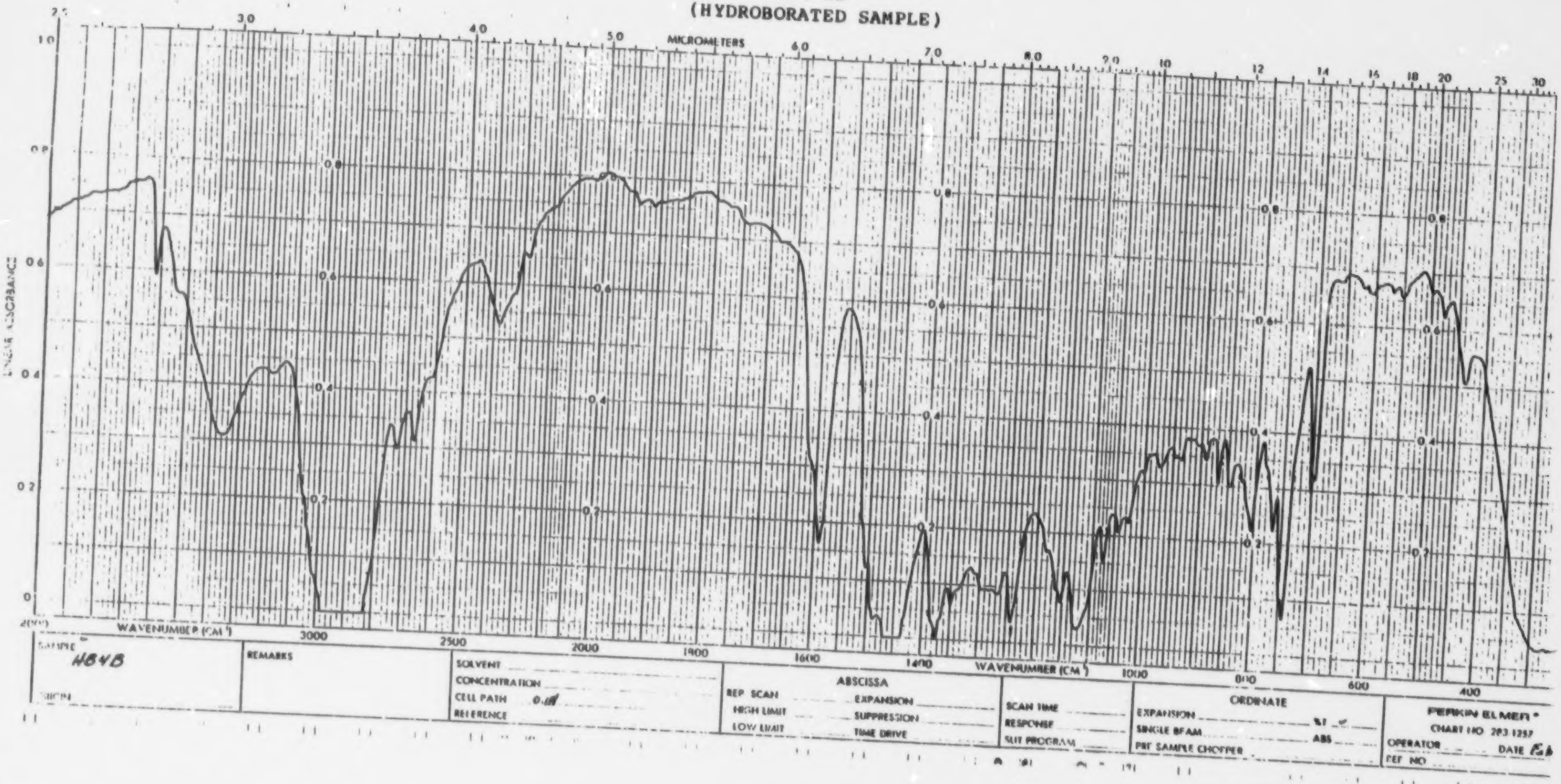


FIGURE 5.4F

WYODAK LIQUIFIED COAL
AP4 HB
(HYDROBORATED SAMPLE)



5.5 Commercial Diesel

Combined Feed = AP5
Saturate Fraction = AP5 (SC)
Hydroborated Fraction = HB AP5

Commercial diesel (166°C to 303°C) was a non-olefinic distillate containing 39 wt.% paraffins (9 wt.% n-paraffin), 35 wt.% cycloparaffin, 22 wt.% aromatics and 4 wt.% resin (Table 5.5B). With the low aromatics content, the cetane index of the sample was 44, exceeding the minimum specification of 40. A summary of ASTM test results was summarized in Table 5.5A.

By LRMS and GCMS (Tables 5.5B, 5.5C), the aromatics in the feed were mainly monoaromatics and the saturates were split equally between paraffins and cycloparaffins. Of the paraffins fraction 9.6 wt.% were n-paraffin with the balance made up of isoparaffins (Table 5.5D). Both LRMS and GCMS results were very similar in paraffin classifications and the GCMS carbon number distribution matched the GC carbon number distribution.

Total ion current (TIC) traces and infrared scans were shown in Figures 5.5A to 5.5C and Figures 5.5D to 5.5F respectively. No olefins were detected by GCMS, IR and bromine number.

TABLE 5.5A

AP4 (COMBINED FEED)
COMMERCIAL DIESEL

Physical Characteristics

Density at 15°C g/cc		0.8205
Aniline Point, °C (ASTM D611)		58.1
Cetane Index (ASTM D976)		44
Cetane Index (CGSB)		43
Nitrogen Content, ppm		20
Sulfur Content, wt%		0.2
Carbon Content, wt%		86
Hydrogen Content, wt%		14
Oxygen Content, wt%		0
Viscosity @ 40°C, ASTM D445 (cSt)		1.5
Distillation, ASTM D86, Vol.%		
°C (GCD wt.%)	IBP	166
	10	187
	20	
	30	
	40	
	50	220
	60	
	70	
	80	
	90	268
	FBP	303
Average Molecular Weight (GCMS)		176
Average Molecular Weight (GCD)		182

TABLE 5.5B

AP5 (AS IS)
COMMERCIAL DIESEL

Components	LRMS	Separation Fractions	Separation Recal. LRMS	GCMS
Weight %				
Saturates	77	77	74	83
Paraffins	40	-	39	42
Cycloparaffins	37	-	35	41
Aromatics	23	19	22	17
Mono-Di	23	17	20	17
Polynuclear	0	2	2	0
Resins	0	4	4	0

TABLE 5.5C

MASS SPECTROMETRY COMPOSITIONAL DATA
COMMERCIAL DIESEL
FEED (AP5) AND SATURATES [AP5 (SC)]

		Feed		Saturates	
	Z Numbers	LRMS	GCMS	LRMS	GCMS
Saturates		77	83	95	100
Paraffins	+2	40	42	50	52
Cycloparaffins		37	41	45	48
Noncond. Cycloparaffins	0	24	28	28	32
Cond. Dicycloparaffins	-2	11	12	14	14
Cond. Polycycloparaffins	-4	2	1	3	2
Aromatics		23	17	5	0
Monoaromatics		19	14	4	0
Alkylbenzenes	-6	14	11	4	0
Benzocycloparaffins	-8	4	3	0	0
Benzodicycloparaffins	-10	1	0	0	0
Diaromatics		4	3	1	0
Naphthalenes	-12	4	3	1	0
Naphthocycloparaffins	-14	0	0	0	0
Fluorenes	-16	0	0	0	0
Triaromatics	-18,-20	0	0	0	0
Tetraaromatics	-22,-24	0	0	0	0
Pentaaromatics	-26,-28,-30	0	0	0	0
Unidentified	-32 to -44	0	0	0	0
Aromatic Sulfurs	-105,-165,-225	0	0	0	0

TABLE 5.5D

PARAFFIN CONTENT
COMMERCIAL DIESEL - AP5(SC)
MASS SPECTROMETRY AND GAS CHROMATOGRAPHY DATA

Components	Feed		Saturates	
	LRMS	GCMS	LRMS	GCMS
Saturates	100	100	100	100
Paraffins	52	50	52	52
Cycloparaffins	48	49	48	48
Noncond. Cycloparaffins	31	34	29	32
Cond. Dicycloparaffins	15	14	15	14
Cond. Polycycloparaffins	3	1	4	2

	GCMS Wt.%	GC Wt.%	GC Wt.%
Normal Paraffins	24.4	23.6	-
Isoparaffins	20.4	-	-
Isoparaffins + Cycloparaffins	-	-	76.5
(% Toluene)	-	4.1	-
Normal Paraffin Distribution Carbon Number			
C8		0.2	0.1
C9	1.4	1.7	2.1
C10	3.5	3.8	10.1
C11	3.9	4.1	12.3
C12	4.1	3.9	12.4
C13	3.4	3.2	12.9
C14	3.3	2.4	10.6
C15	2.1	2.1	7.9
C16	1.3	1.2	4.7
C17	0.7	0.6	2.3
C18	0.3	0.2	0.9
C19	0.2	0.1	0.2
C20	0.2	0.1	0.0

TABLE 5.5E

OLEFIN CONTENT
COMMERCIAL DIESEL - HB AP5

	HB AP5
Average MW (GCMS)	176
IR Wt.% OH	0
GCMS: wt. % TMS Ether	0
Bromine Number: wt.% Olefin	0

87 wt.% recovery of hydroborated sample

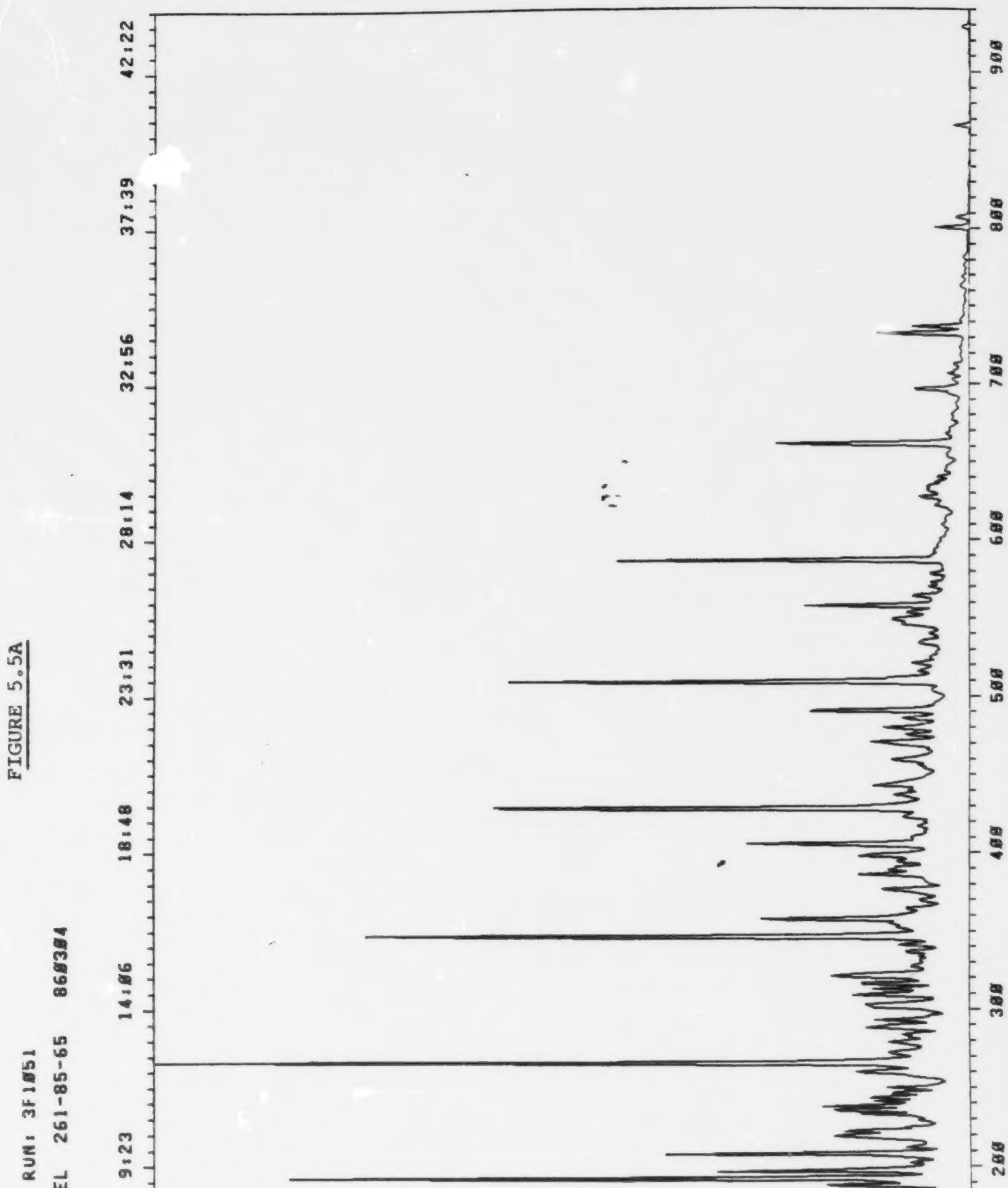
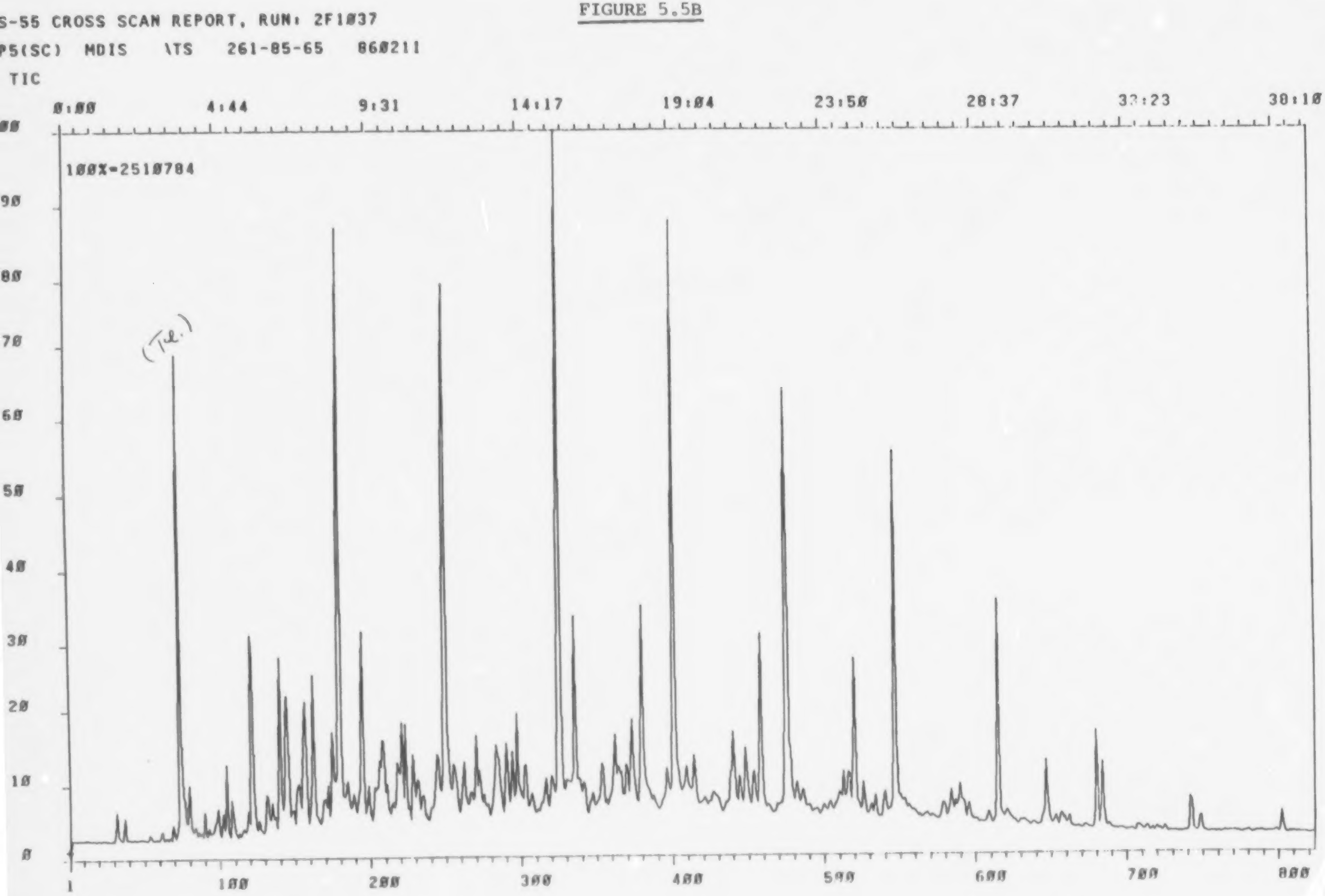


FIGURE 5.5A

05-05 CROSS SCAN REPORT, RUN: 3F1051
AP5 COMPOSITE COMM. DIESEL 261-85-65 860304
+ TIC
100%=2765312
2:19
4:41
9:23
14:06
18:48
23:31
28:14
32:56
37:39
42:22
100
90
80
70
60
50
40
30
20
10
0
50
100
200
300
400
500
600
700
800
900

FIGURE 5.5B


S-55 CROSS SCAN REPORT, RUN: 2F1037
P5(SC) MDIS \TS 261-85-65 860211
TIC
0:00
4:44
9:31
14:17
19:04
23:50
28:37
33:23
38:10
100%=2510784
(Tl.)
00
90
80
70
60
50
40
30
20
10
0
1
100
200
300
400
500
600
700
800

DS-55 CROSS SCAN REPORT, RUN: 3F1064
HB5B(1) COMMERCIAL DIESEL 261-05-65 860331
* 73 , 75 + TIC

FIGURE 5.5C

Graph 11

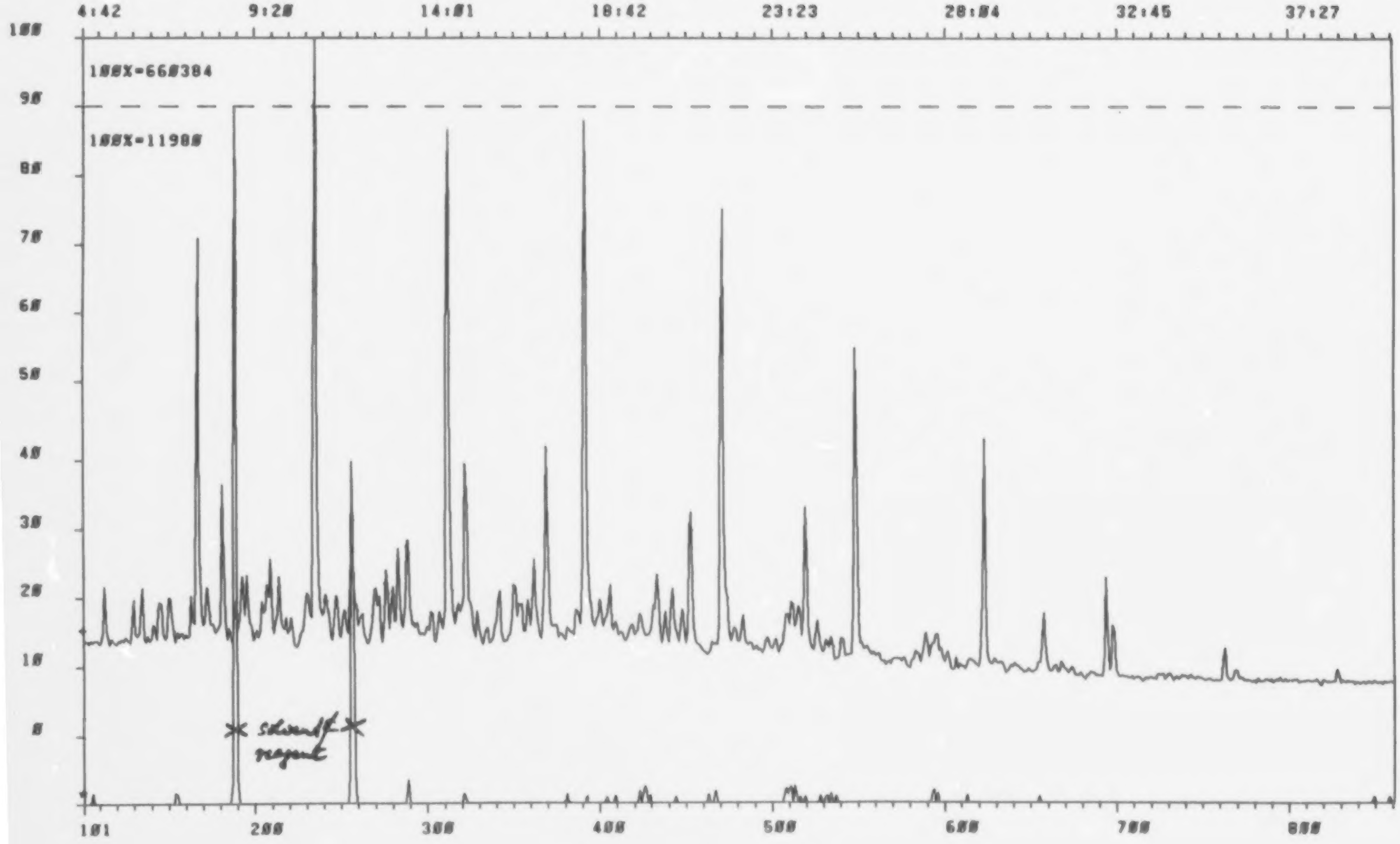
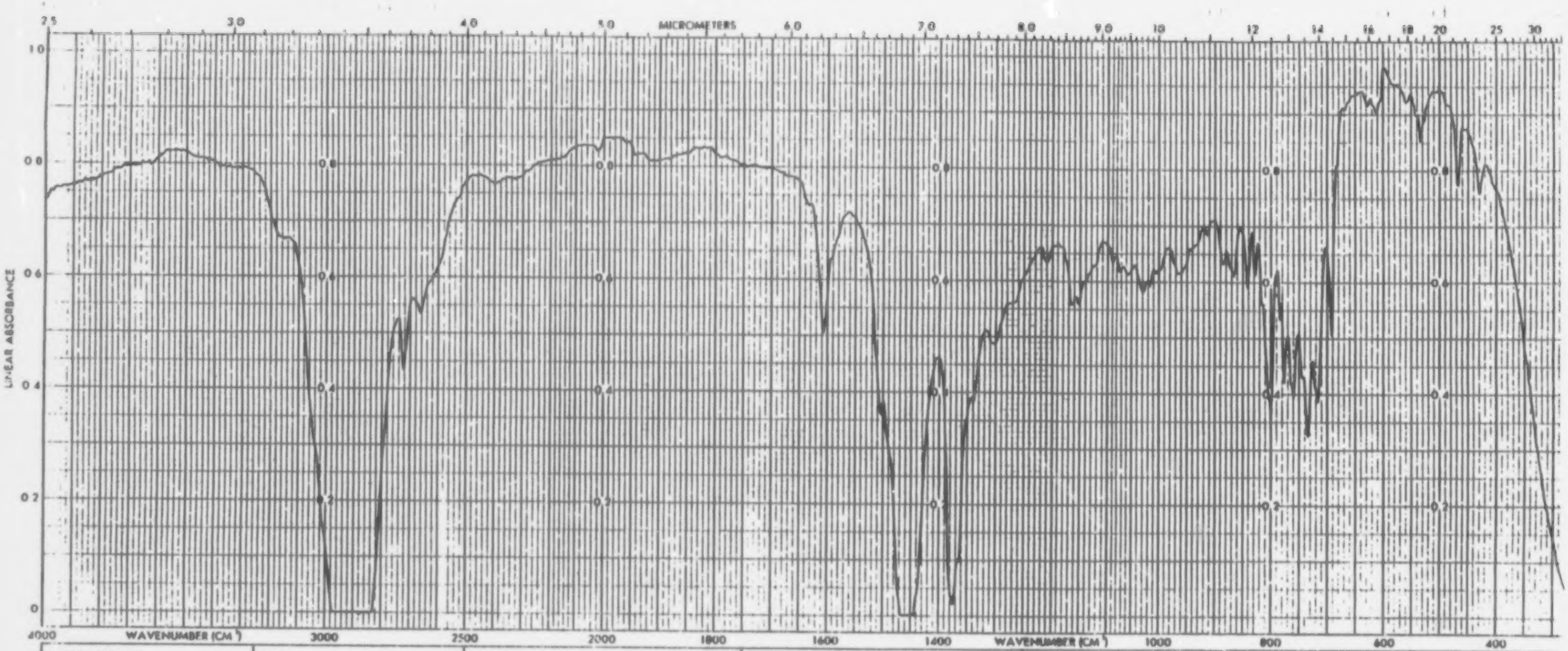


FIGURE 5.5D

MONTREAL COMMERCIAL DIESEL
AP5
(SAMPLE AS IS)



SAMPLE AP5
Montreal Commercial Diesel
ORIGIN MRS-10-1

REMARKS

SOLVENT
CONCENTRATION
CELL PATH 0.031
REFERENCE

ABSCISSA
REP SCAN
EXPANSION
HIGH LIMIT
SUPPRESSION
LOW LIMIT
TIME DRIVE

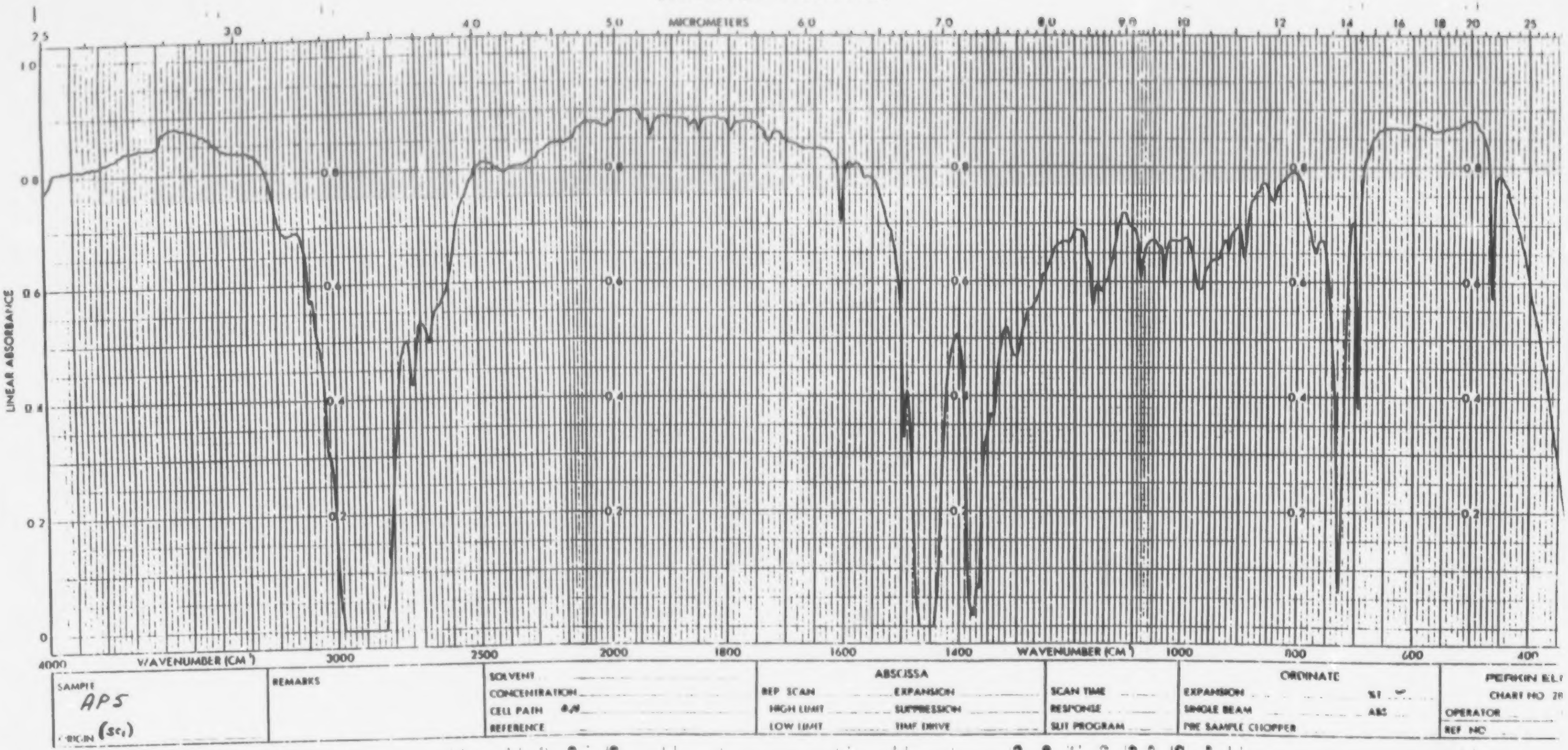
SCAN TIME
RESPONSE
SLIT PROGRAM

ORDINATE
EXPANSION
%T
SINGLE BEAM
ABS
PRE SAMPLE CHOPPER

PERKIN-ELMER
CHART NO. 283 1257
OPERATOR
DATE
REF NO

FIGURE 5.5E

MONTREAL COMMERCIAL DIESEL
AP5 Sc
(SATURATE FRACTION)

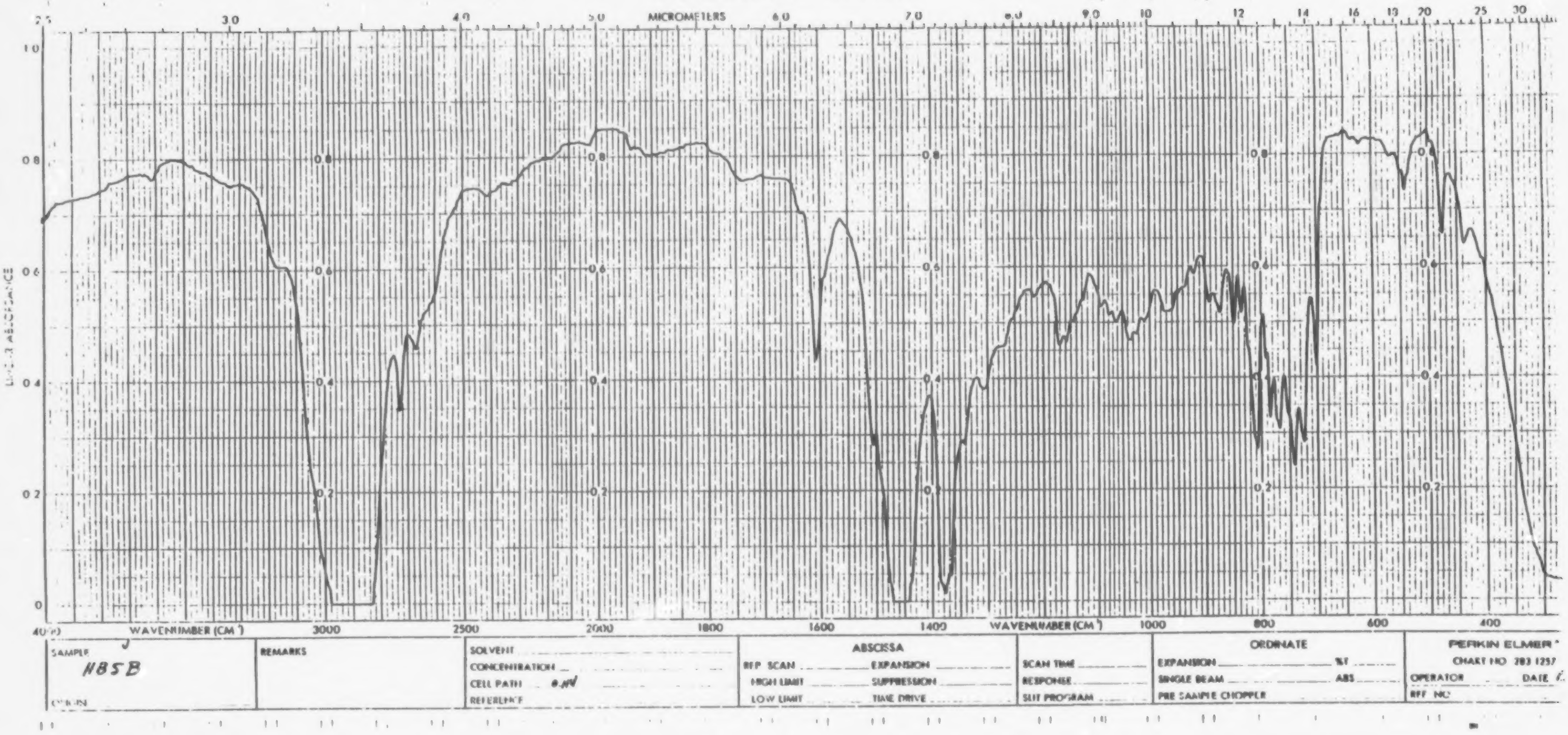


SAMPLE AP5

ORIGIN (sc₁)

FIGURE 5.5F

MONTREAL COMMERCIAL DIESEL
AP5 HB
(HYDROBORATED SAMPLE)



5.6 Syncrude EFV O/H

Combined Feed = AP6
Saturate Fraction = AP6 (SC)
Hydroborated Fraction = HB AP6

Syncrude EFV O/H was a 252°C to 346°C olefinic distillate containing 3 wt.% paraffins (0.1 wt.% n-paraffin) 41 wt.% cycloparaffins, 45 wt.% aromatics and 11 wt.% resins (Table 5.6B). The hydrocarbons identified as resins by hydrocarbon separation method were classified as cycloparaffins by LRMS and GCMS. This is illustrated in Table 5.6B where adding the 11 wt.% resins to the cycloparaffins in the third column (Recal LRMS) would give a total saturate fraction of 55 wt.% (half way between 50 wt.% by LRMS feed and 63 wt.% by GCMS). The low cetane index (Table 5.6A) of 34 reflects the low saturate content and the high aromatics (Table 5.6C).

The saturate fraction of the composite (44 wt.%) was mainly cycloparaffins (41 wt.%) with a small amount of paraffins. Although very small, n-paraffins analyzed by GCMS agreed with carbon number distribution by the GC method (Table 5.5D).

The total ion current (TIC) traces and infrared scans were shown in Figures 5.6A to 5.6C and Figures 5.6D to 5.6F respectively.

The GCMS spectra (Figure 5.6C2) showed intense molecular ions for TMS ethers of C_{12}-C_{18} (Z0) olefins and weak molecular ions for C_{14}-C_{18}, (Z-2 and Z-4) cyclic olefins. Several weak molecular ions for benzothiophene TMS ethers were also observed. The estimated TMS ether concentration by GCMS of 20 wt.% does not compare with the OH content by I.R. at 6% but is similar to the 25 wt.% olefinic components determined by bromine number.

TABLE 5.6A

AP6 (COMBINED FEED)
SYNCRUDE EFV O/H

Physical Characteristics

Density at 15°C g/cc	0.9245
Aniline Point, °C (ASTM D611)	37.6
Cetane Index (ASTM D976)	34
Cetane Index (CGSB)	28
Nitrogen Content, ppm	400
Sulfur Content, wt%	3
Carbon Content, wt%	85
Hydrogen Content, wt%	12
Oxygen Content, wt%	0
Viscosity @ 40°C, ASTM D445 (cSt)	6.8
Distillation, ASTM D86, Vol.%	
°C (GCD wt.%) IBP	252
10	276
20	286
30	293
40	299
50	305
60	311
70	318
80	325
90	333
FBP	346
Average Molecular Weight (GCMS)	226
Average Molecular Weight (GCD)	253

TABLE 5.6B

AP5 (AS IS)
SYNCRUDE EFV OVERHEAD

Components	LRMS	Separation Fractions	Recal. LRMS	GCMS
Weight %				
Saturates	50	52	44	63
Paraffins	2	-	3	4
Cycloparaffins	48	-	41	59
Aromatics	50	37	45	37
Mono-Di	38	30	31	31
Polynuclear	12	7	14	6
Resins	0	11	11	0

TABLE 5.6C

MASS SPECTROMETRY COMPOSITIONAL DATA
SYNCRUDE EFV O/H
FEED (AP6) AND SATURATES [AP6 (SC)]

	Z Numbers	Feed LRMS	Feed GCMS	Saturates LRMS	Saturates GCMS
Saturates		50	63	84	88
Paraffins	+2	2	4	6	5
Cycloparaffins		48	59	78	83
Noncond. Cycloparaffins	0	17	24	29	33
Cond. Dicycloparaffins	-2	17	20	30	31
Cond. Polycycloparaffins	-4	14	15	19	19
Aromatics		50	37	16	12
Monoaromatics		24	21	11	9
Alkylbenzenes	-6	7	8	6	5
Benzocycloparaffins	-8	8	6	3	2
Benzodicycloparaffins	-10	9	7	2	2
Diaromatics		14	9	2	0
Naphthalenes	-12	6	5	0	0
Naphthocycloparaffins	-14	4	2	0	0
Fluorenes	-16	4	2	2	0
Triaromatics	-18,-20	3	1	2	1
Tetraaromatics	-22,-24	1	1	1	1
Pentaaromatics	-26,-28,-30	0	0	0	0
Unidentified	-32 to -44	0	0	0	0
Aromatic Sulfurs	-105,-165,-225	8	5	2	1

TABLE 5.6D

PARAFFIN CONTENT
SYNCRUDE EFV OVERHEAD - AP6(SC)
MASS SPECTROMETRY AND GAS CHROMATOGRAPHY DATA

Components	Feed		Saturates	
	LRMS	GCMS	LRMS	GCMS
Saturates	100	100	100	100
Paraffins	4	6	7	6
Cycloparaffins	96	94	93	94
Noncond. Cycloparaffins	34	38	34	37
Cond. Dicycloparaffins	34	32	35	36
Cond. Polycycloparaffins	28	24	24	21

	GCMS Wt.%	GC Wt.%	GC Wt.%
Normal Paraffins	1.4	2.1	-
Isoparaffins	1.0	-	-
Isoparaffins + Cycloparaffins	-	-	97.9
(% Toluene)	-	0.2	-
Normal Paraffin Distribution Carbon Number			
C12	-	-	0.7
C13	0.1	0.1	3.0
C14	0.3	0.3	4.5
C15	0.4	0.6	9.4
C16	0.2	0.2	12.8
C17	0.2	0.3	17.0
C18	0.1	0.2	16.4
C19	0.1	0.1	11.0
C20	0.0	0.1	10.6
C21	-	0.1	7.5
C22	-	0.1	4.1
C23	-	0.0	0.9

TABLE 5.6E

OLEFIN CONTENT
SYNCRUDE EFV O/H - HB AP6

	HB AP5
Average MW (GCMS)	226
IR Wt.% OH	6
GCMS: wt. % TMS Ether	20
Bromine Number: wt.% Olefin	25

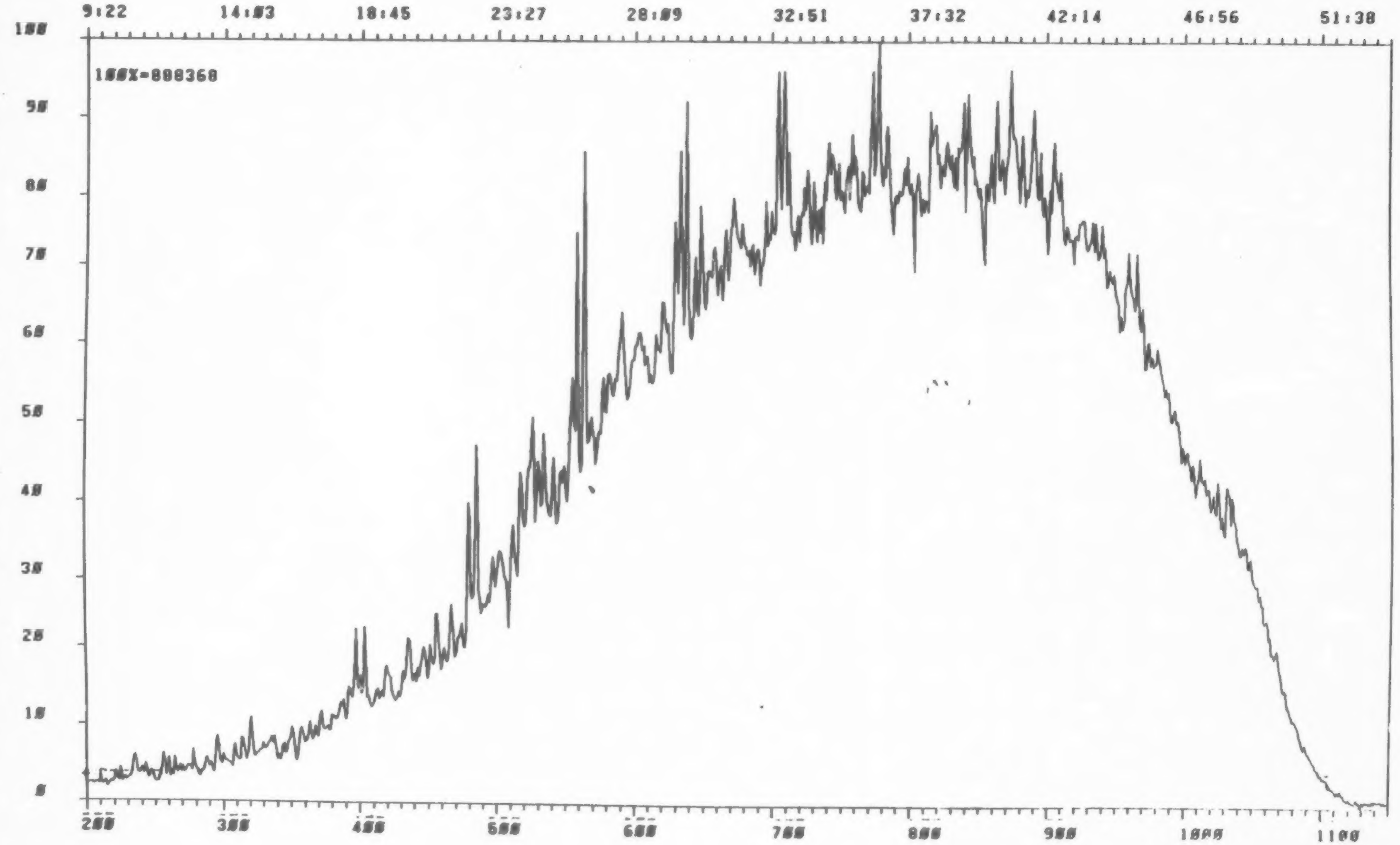
98 wt.% recovery of hydroborated sample

FIGURE 5.6A

DS-55 CROSS SCAN REPORT, RUN: 3F1056

AP6 COMPOSITE SYNCRUDE EFV O/H 252-346C 261-85-65

+ TIC



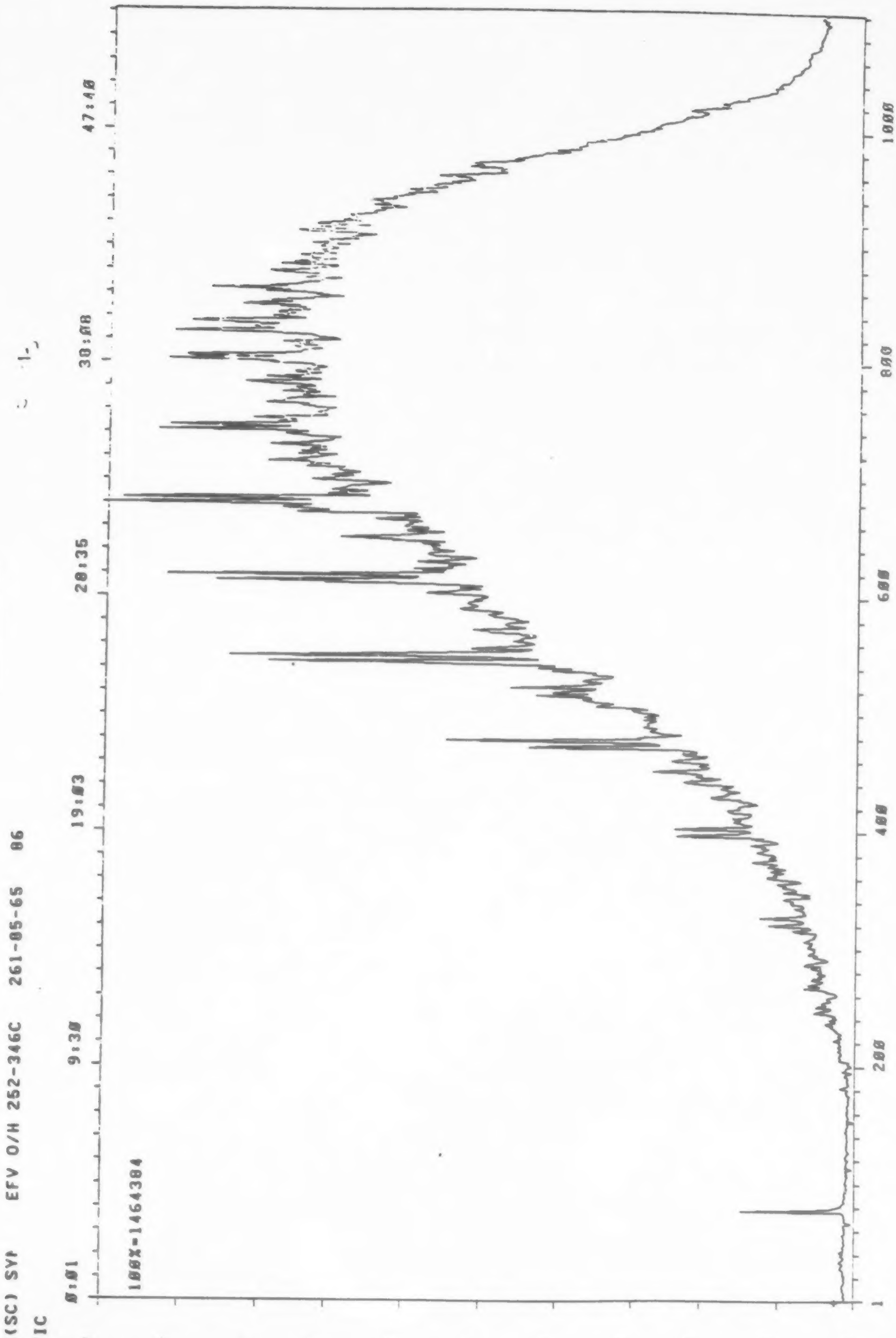

AP6(SC) SYt EFV O/H 252-346C 261-05-65 06
+ TIC
100X-1464384
0:01
9:30
19:03
28:35
38:08
47:40
100
90
80
70
60
50
40
30
20
10
0
1
200
400
600
800
1000

FIGURE 5.6B

FIGURE 5.6C1

Graph 5

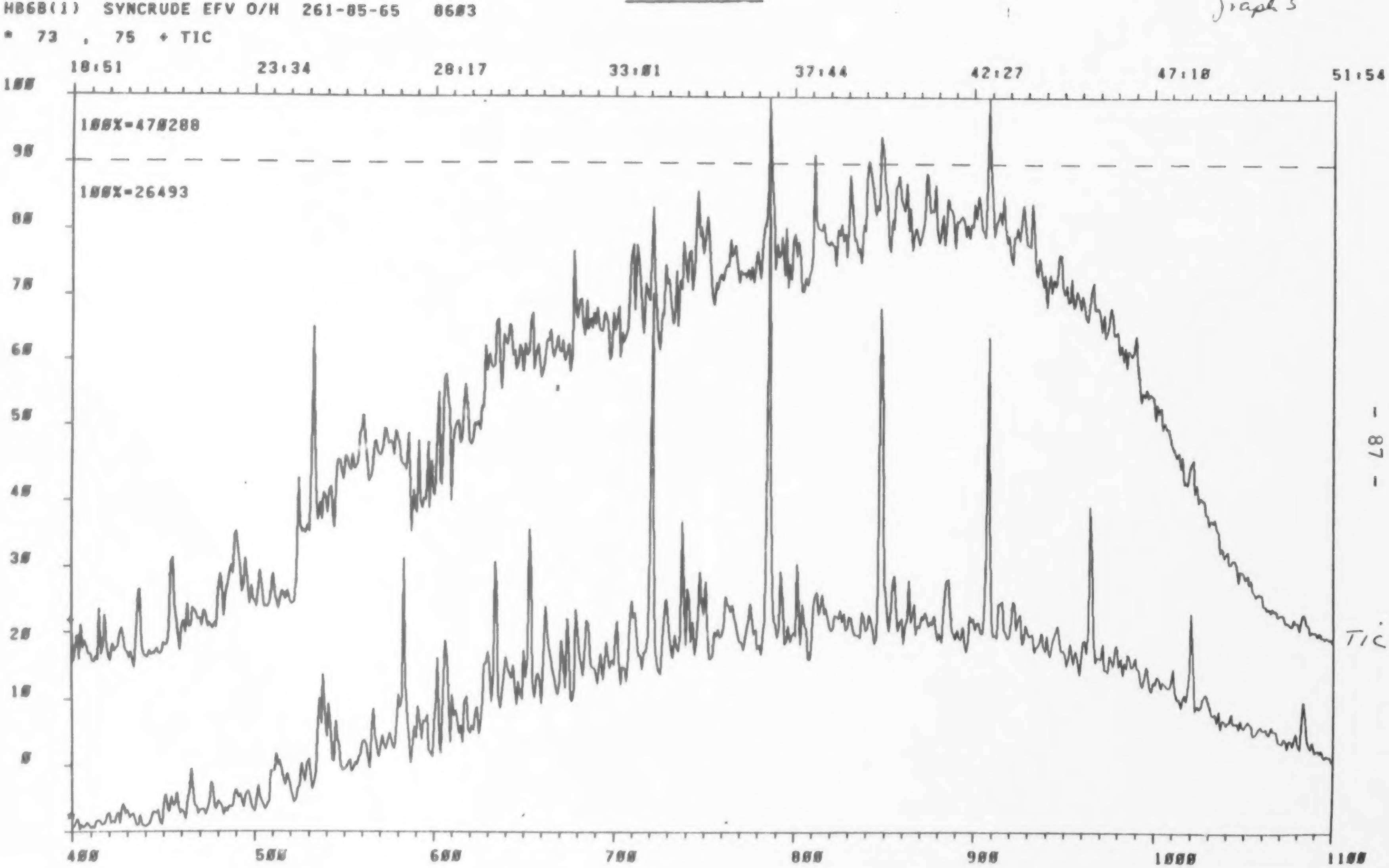


FIGURE 5.6 C2

[illegible] 6

HB6B(1) SYNCRUDE EFV O/H 261-85-65 860331
* 340 # 326 O 312 & 298 $ 284 X 270 + TIC

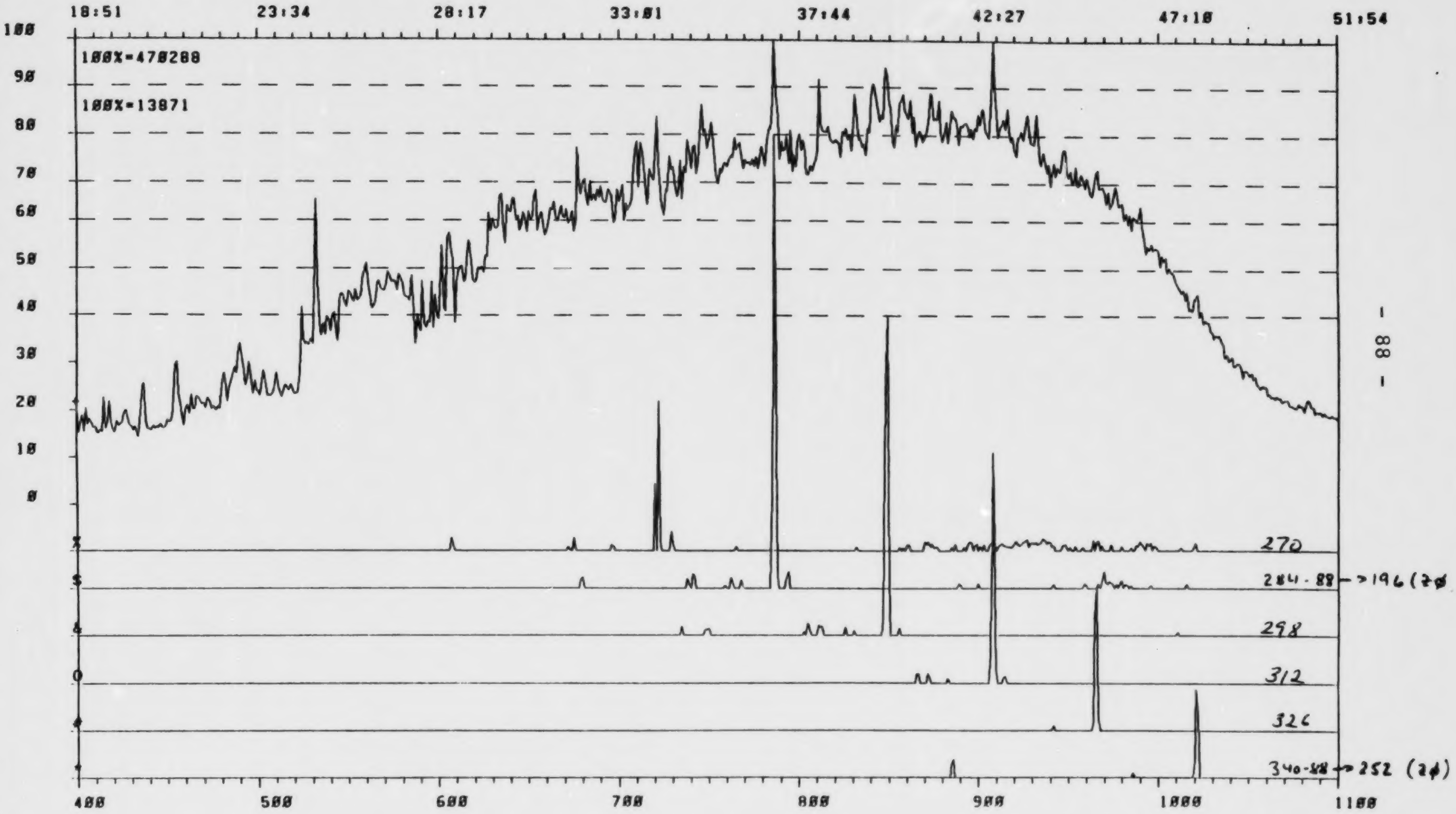


FIGURE 5.6D

SYNCRUDE EFV O/H
AP6
(SAMPLE AS IS)

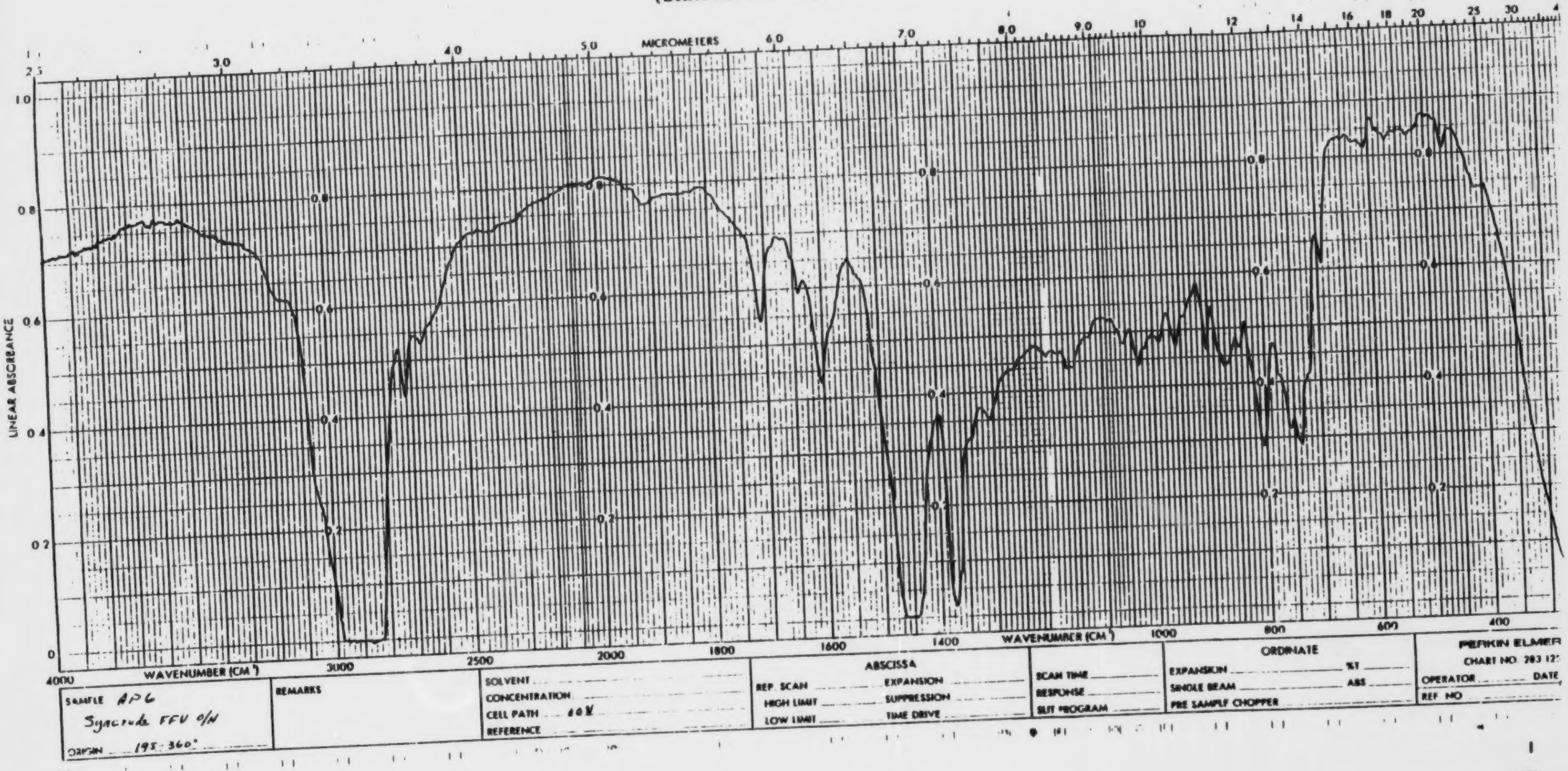


FIGURE 5.6E
SYNCRUDE EFV O/H
AP6 Sc
(SATURATE FRACTION)

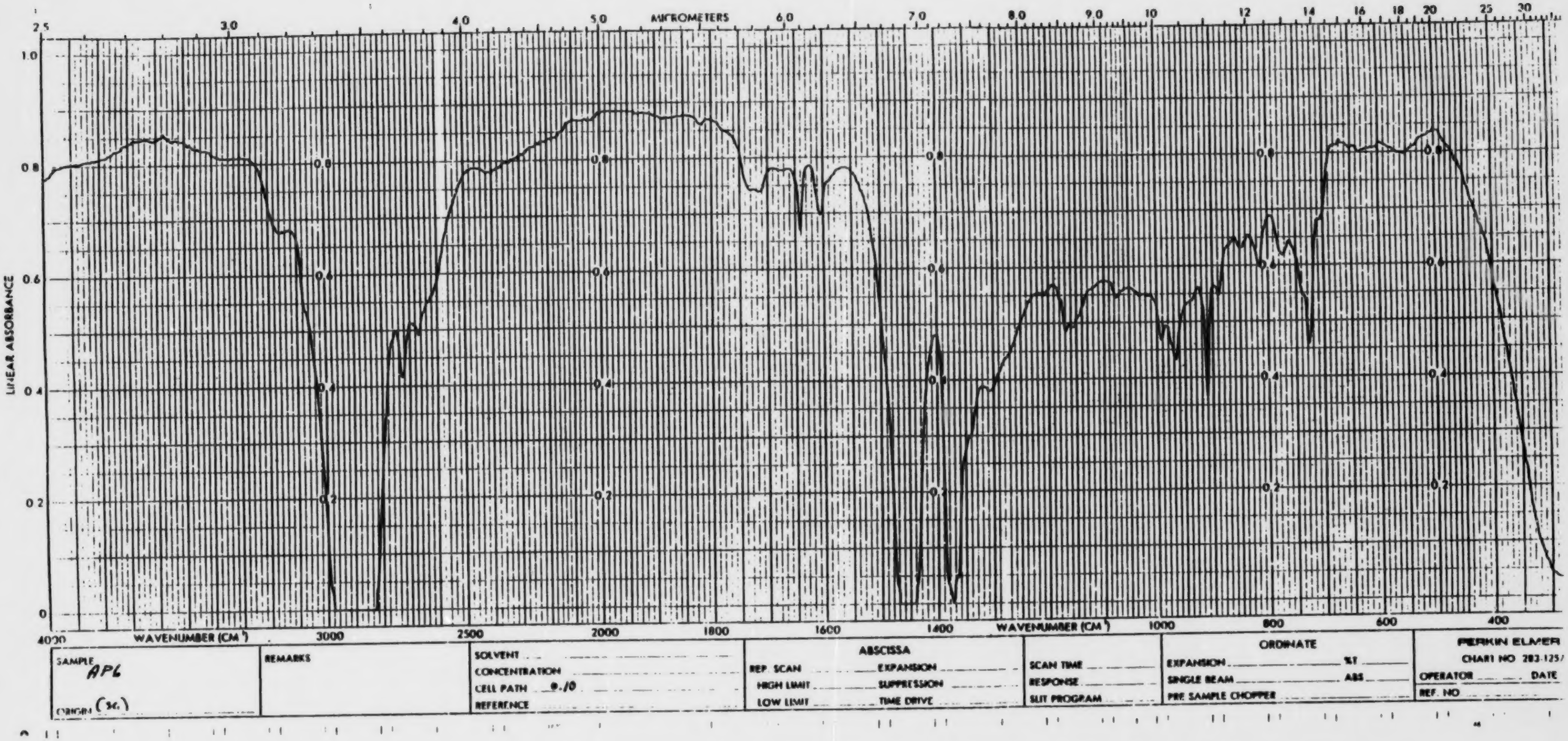
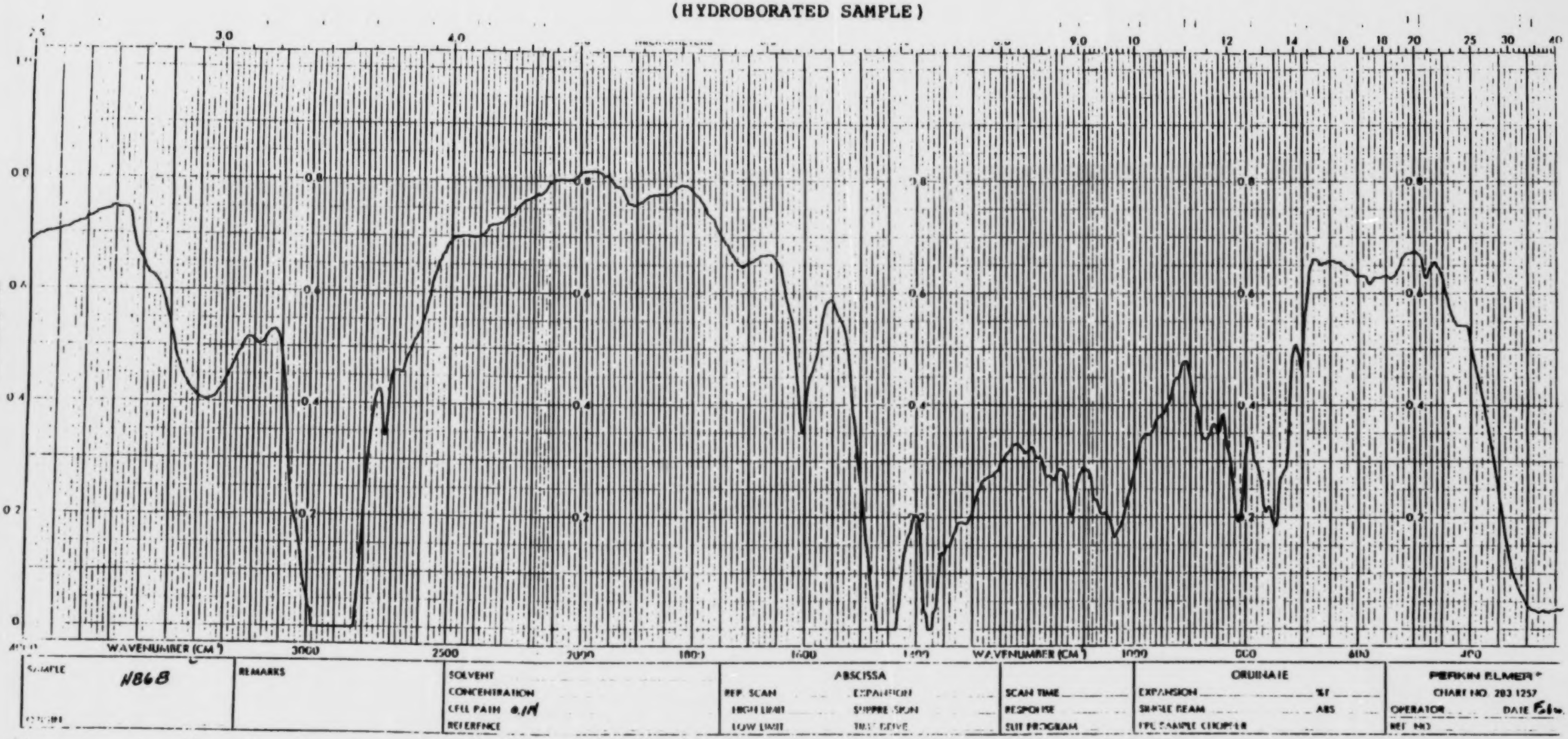


FIGURE 5.6F

SYNCRUDE EFV O/H
AP6 HB
(HYDROBORATED SAMPLE)



5.7 Edmonton Coker Distillate

Combined Feed = AP7
Saturate Fraction = AP7 (SC)
Hydroborated Fraction = HB AP7

The Edmonton Coker Distillate (162°C to 277°C) was olefinic containing 31 wt.% paraffins (9 wt.% n-paraffin), 35 wt.% cycloparaffins, 27 wt. % aromatics and 7 wt.% resins (Table 5.7B). Physical characteristics (Table 5.7A) such as cetane number met the 40 minimum reading. By LRMS and GCMS (Table 5.7B, 5.7C) the aromatics in the feed were mainly monoaromatics and the saturates were split equally between paraffins and cycloparaffins. GCMS n-paraffin concentrations given in Table 5.7D agreed well with GC values illustrating repeatability.

The total ion current (TIC) traces and infrared scans were shown in Figures 5.7A to 5.7C and Figures 5.6D to 5.6F respectively. Figure 5.7A showed the TIC envelope and E73 and E75 ion plot of this sample. The GCMS spectra showed intense molecular ions that correspond to Z-2, C_{10}-C_{13} cyclic olefins and Z-10, C_9-C_{11}.

The TMS ether concentration by GCMS was estimated at 38 wt. % and although much higher than the OH content by IR (14), it related well to the potential olefin concentration of 40 wt.% olefin by bromine number.

TABLE 5.7A

AP6 (COMBINED FEED)
EDMONTON COKER DISTILLATE

Physical Characteristics

Density at 15°C g/cc		0.8295
Aniline Point, °C (ASTM D611)		48.5
Cetane Index (ASTM D976)		42
Cetane Index (CGSB)		37
Nitrogen Content, ppm		250
Sulfur Content, wt%		0.3
Carbon Content, wt%		86
Hydrogen Content, wt%		13
Oxygen Content, wt%		0
Viscosity @ 40°C, ASTM D445 (cSt)		1.6
Distillation, ASTM D86, Vol.%		
°C (GCD wt.%)	IBP	162
	10	193
	20	203
	30	210
	40	217
	50	224
	60	231
	70	239
	80	247
	90	257
	FBP	277
Average Molecular Weight (GCMS)		184
Average Molecular Weight (GCD)		182

TABLE 5.7B

AP5 (AS IS)
EDMONTON COKER MIDDLE DISTILLATE

Components	LRMS	Separation Fractions	Separation Recal. LRMS	GCMS
Weight %				
Saturates	73	76	66	79
Paraffins	33	-	31	39
Cycloparaffins	40	-	35	40
Aromatics	27	17	27	21
Mono-Di	27	16	26	21
Polynuclear	0	1	1	0
Resins	0	7	7	0

TABLE 5.7C

MASS SPECTROMETRY COMPOSITIONAL DATA
EDMONTON COKER DISTILLATE
FEED (AP7) AND SATURATES [AP7 (SC)]

		Feed		Saturates	
	Z Numbers	LRMS	GCMS	LRMS	GCMS
Saturates		73	79	87	98
Paraffins	+2	33	39	40	47
Cycloparaffins		40	40	47	51
Noncond. Cycloparaffins	0	22	25	26	29
Cond. Dicycloparaffins	-2	10	12	13	14
Cond. Polycycloparaffins	-4	8	3	8	8
Aromatics		27	21	12	2
Monoaromatics		22	17	12	1
Alkylbenzenes	-6	11	10	0	1
Benzocycloparaffins	-8	8	6	0	0
Benzodicycloparaffins	-10	3	1	0	0
Diaromatics		5	4	0	0
Naphthalenes	-12	5	4	0	0
Naphthocycloparaffins	-14	0	0	0	0
Fluorenes	-16	0	0	0	0
Triaromatics	-18,-20	0	0	0	0
Tetraaromatics	-22,-24	0	0	0	0
Pentaaromatics	-26,-28,-30	0	0	0	0
Unidentified	-32 to -44	0	0	0	0
Aromatic Sulfurs	-105,-165,-225	0	0	0	0

TABLE 5.7D

PARAFFIN CONTENT
EDMONTON COKER DISTILLATE - AP7(SC)
MASS SPECTROMETRY AND GAS CHROMATOGRAPHY DATA

Components	Feed		Saturates	
	LRMS	GCMS	LRMS	GCMS
Saturates	100	100	100	100
Paraffins	45	49	46	47
Cycloparaffins	55	51	54	53
Noncond. Cycloparaffins	30	32	30	30
Cond. Dicycloparaffins	14	15	15	14
Cond. Polycycloparaffins	11	4	9	9

	GCMS Wt.%	GC Wt.%	GC Wt.%
Normal Paraffins	30.0	25.1	-
Isoparaffins	12.1	-	-
Isoparaffins + Cycloparaffins	-	-	74.9
(% Toluene)	-	11.7	-
Normal Paraffin Distribution Carbon Number			
C8	-	0.3	0.3
C9	0.8	0.6	1.3
C10	2.4	2.3	4.4
C11	4.4	4.2	10.1
C12	6.0	4.8	12.6
C13	5.1	4.3	14.3
C14	5.3	3.8	12.9
C15	4.0	3.1	11.2
C16	1.7	1.4	5.8
C17	0.3	0.3	1.8
C18	-	-	0.2

TABLE 5.7E

OLEFIN CONTENT
EDMONTON COKER DISTILLATE - HB AP7

	HB AP7
Average MW (GCMS)	184
IR Wt.% OH	13
GCMS: wt. % TMS Ether	38
Bromine Number: wt.% Olefin	40

85 wt.% recovery of hydroborated sample

FIGURE 5.7A

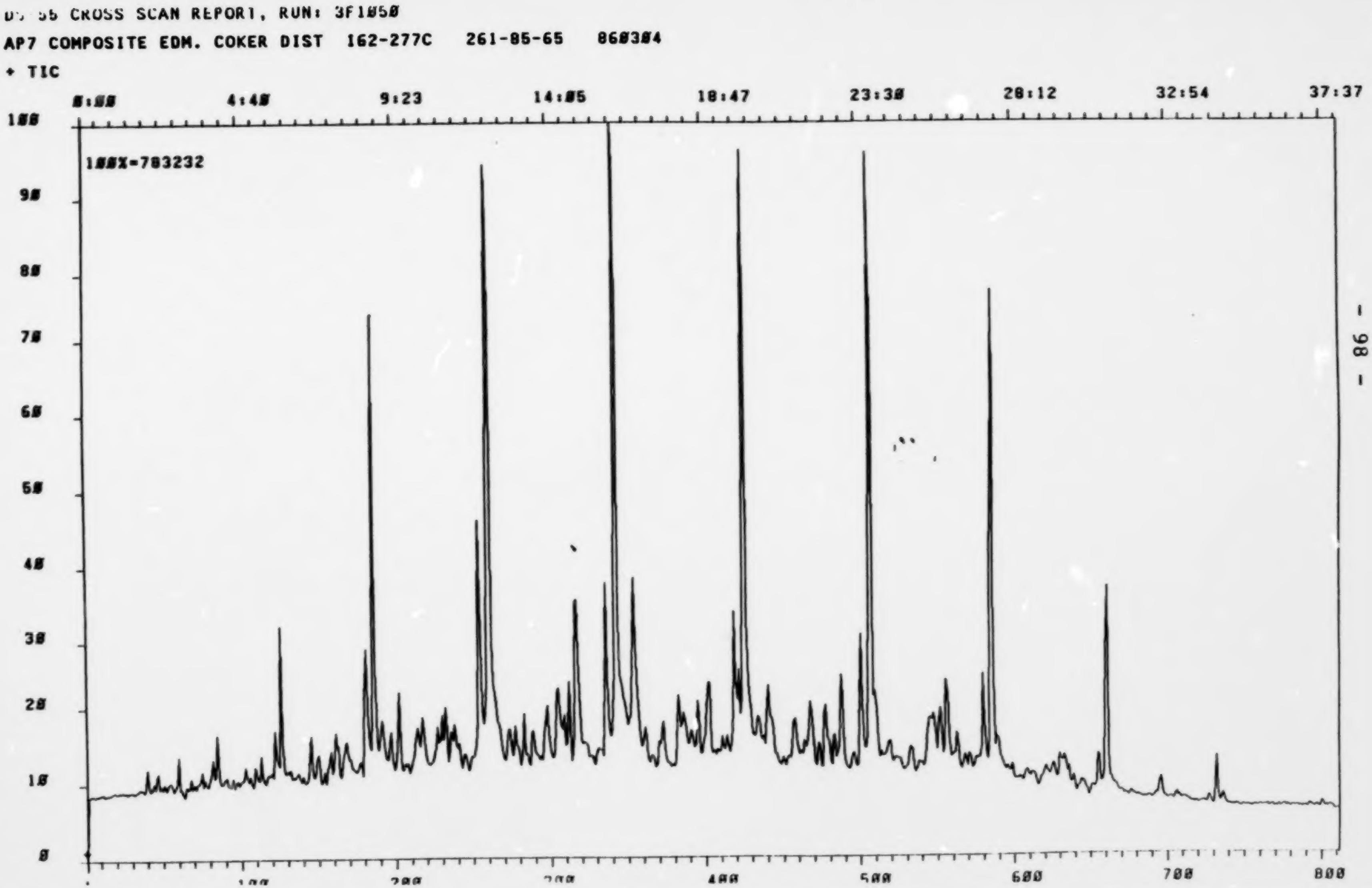

D 55 CROSS SCAN REPORT, RUN: 3F1050
AP7 COMPOSITE EDM. COKER DIST 162-277C 261-85-65 860304
+ TIC
0:00
4:40
9:23
14:05
18:47
23:30
28:12
32:54
37:37
100
90
80
70
60
50
40
30
20
10
0
100%=783232
100
200
300
400
500
600
700
800

FIGURE 5.7B

DS-55 CROSS SCAN REPORT, RUN: 2F1038
AP7(SC) EDM OKER SATS 261-85-65 860211
+ TIC

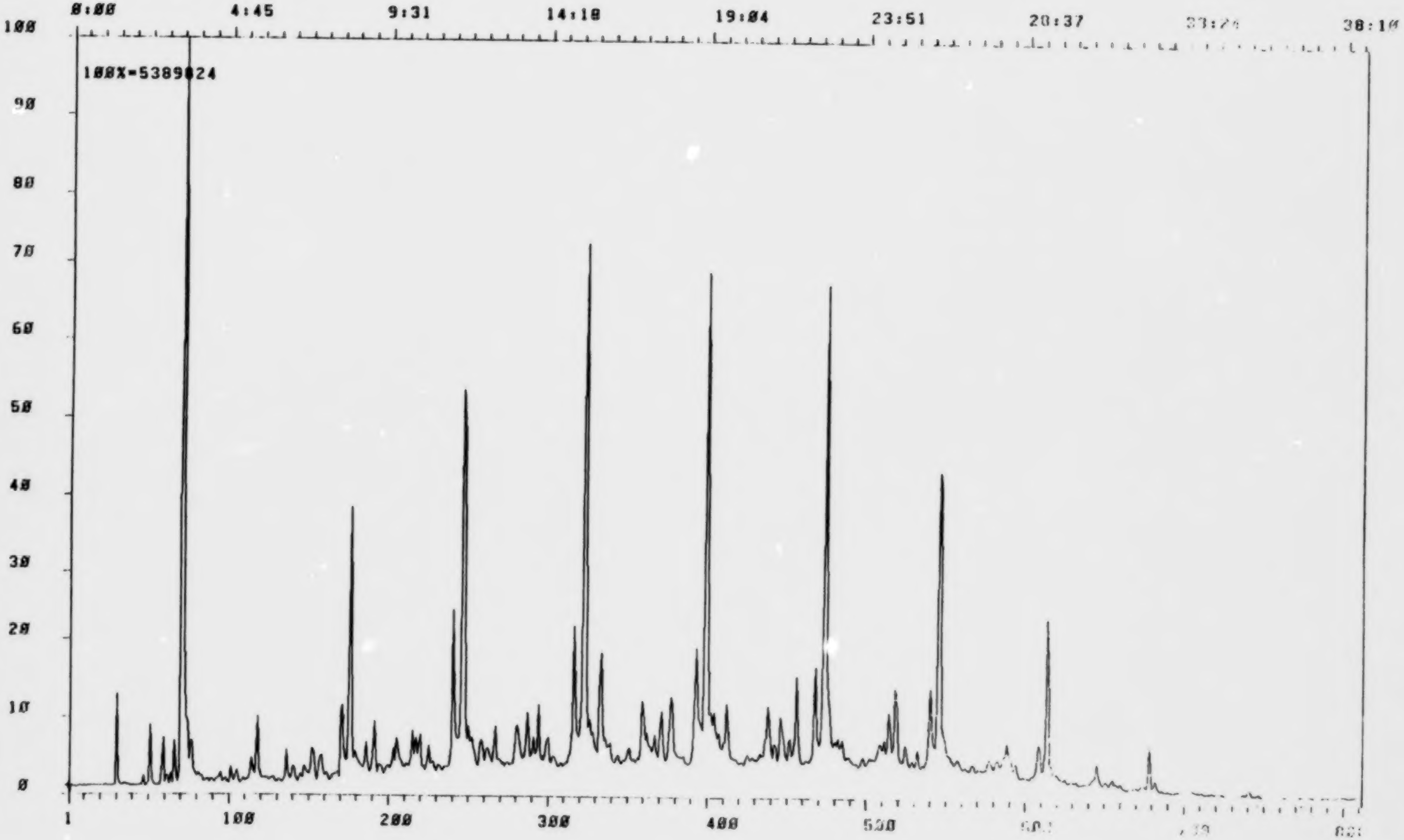


FIGURE 5.7 C1

Graph 7

DS-55 CROSS SCAN REPORT, RUN: 3F1065
HB7B(2) EDMONTON COKER DIST 261-85-65 8603
* 73 , 75 + TIC

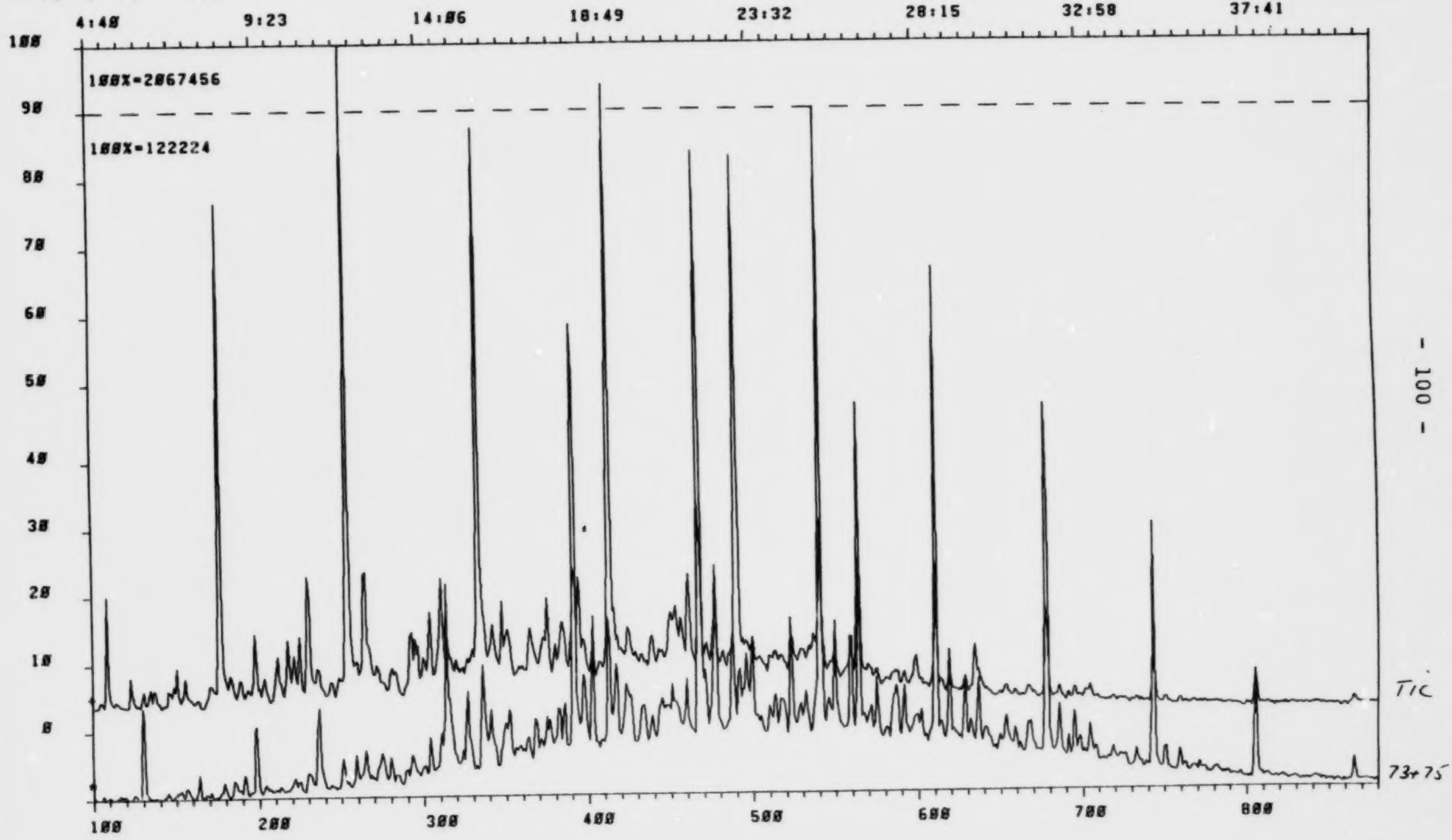
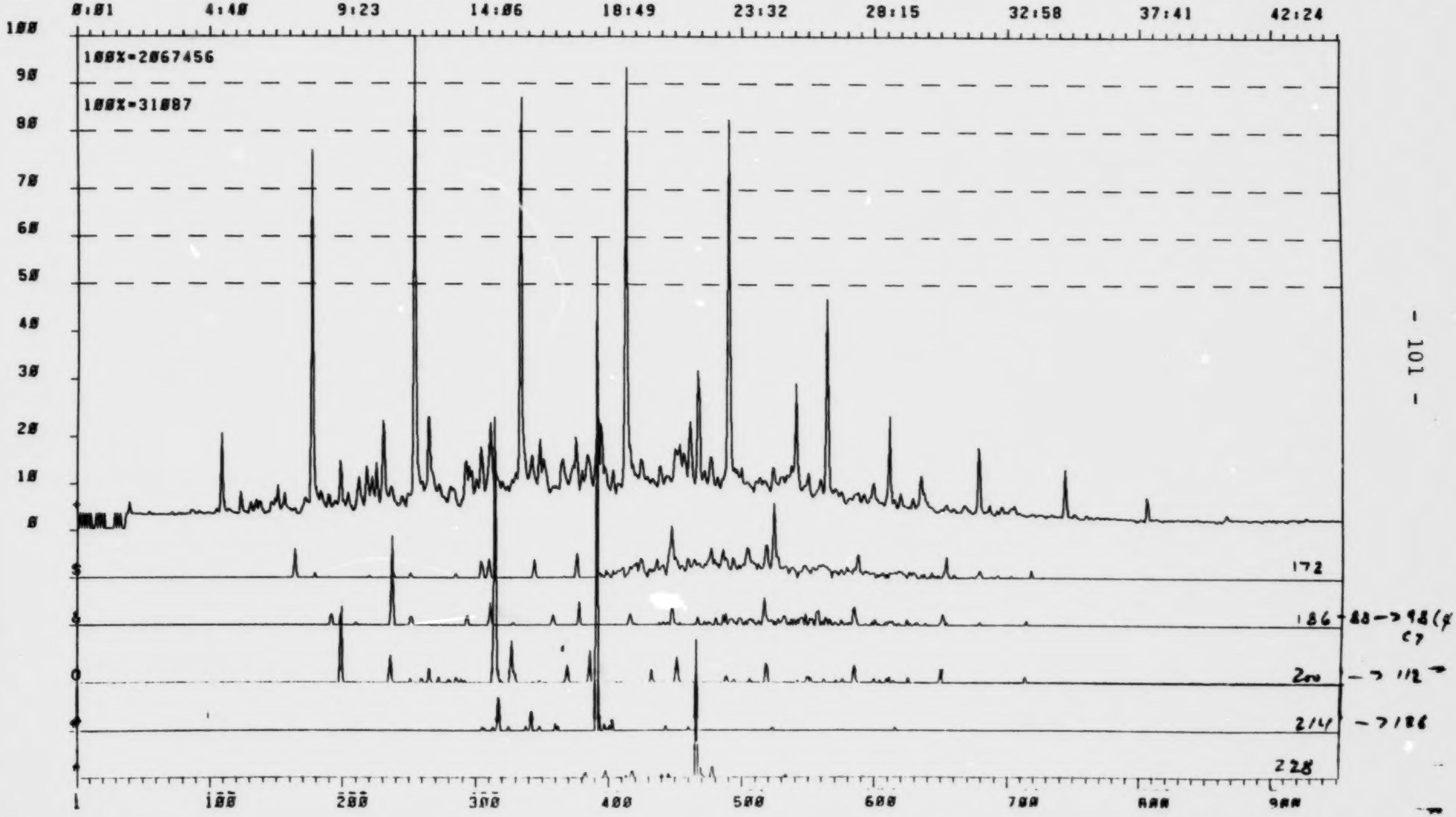


FIGURE 5.7 C2

DS-55 CROSS SCAN REPORT, RUN: 3F1065
HB78(2) EDMONTON COKER DIST 261-85-65
* 229 # 215 O 201 & 187 $ 173 + TIC

Graph 8
(see 8a)



Graph 8a

FIGURE 5.7 C3

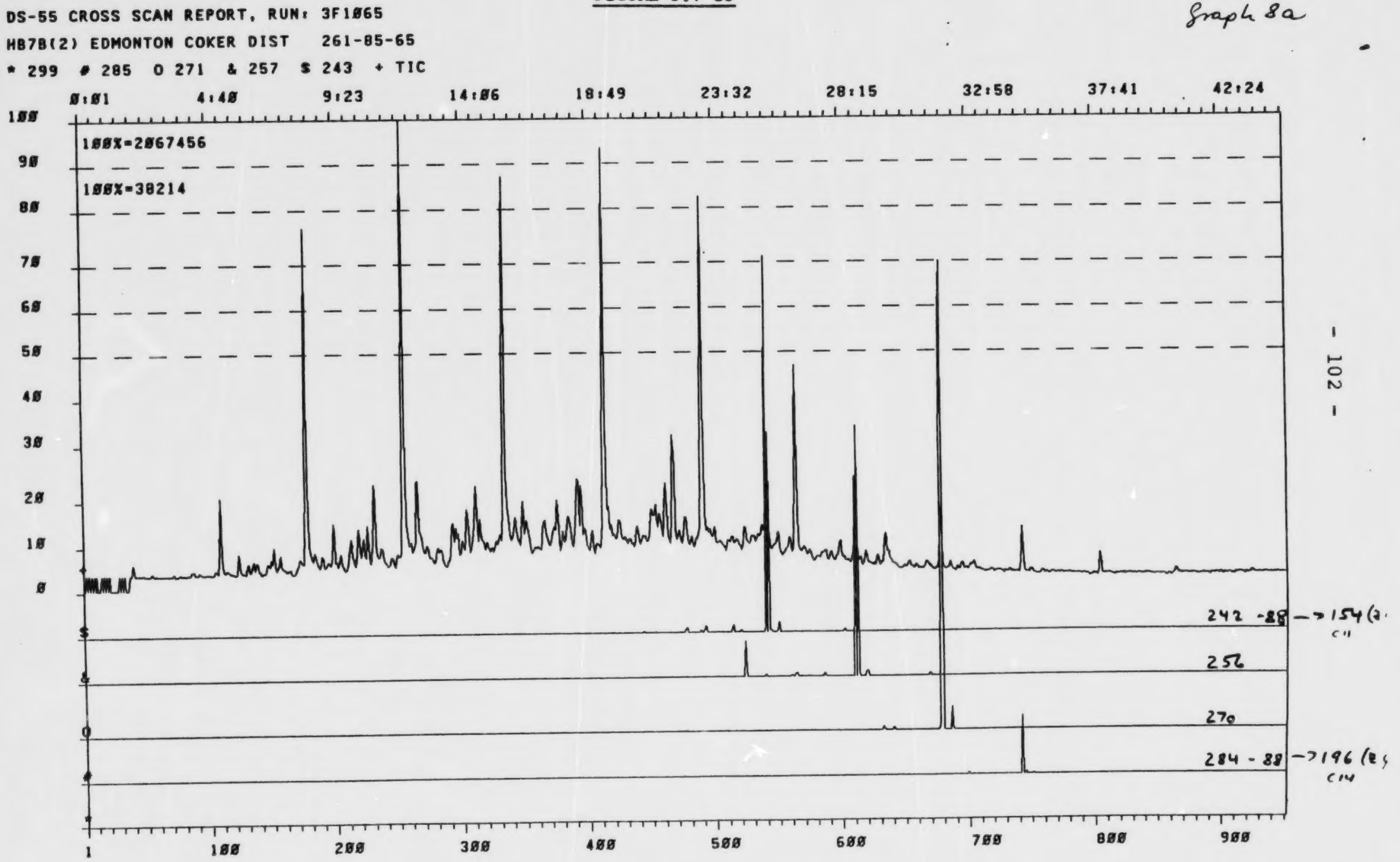
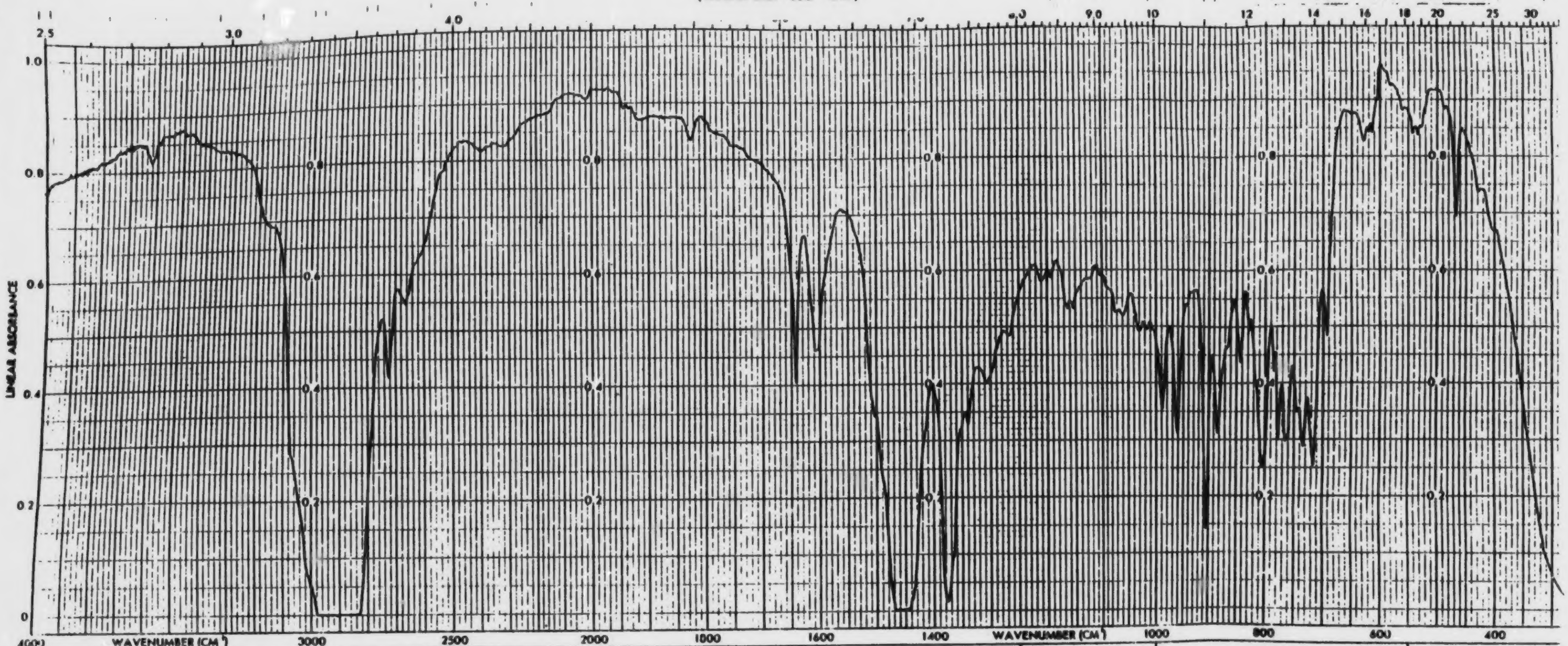


FIGURE 5.7D

EDMONTON COKER DISTILLATE
AP7
(SAMPLE AS IS)



SAMPLE AP7
Edmonton Coker Distillate
ORIGIN E-144-78

REMARKS

SOLVENT
CONCENTRATION
CELL PATH 0.125 mm
REFERENCE

ABSCISSA
REP. SCAN
EXPANSION
HIGH LIMIT
SUPPRESSION
LOW LIMIT
TIME DRIVE

SCAN TIME 24
RESPONSE
SLIT PROGRAM

ORDINATE
EXPANSION
%T ✓
SINGLE BEAM
ABS
PRE SAMPLE CHOPPER

PERKIN ELMER
CHART NO 283-1257
OPERATOR
DATE
REF. NO.

FIGURE 5.7 E

EDMONTON COKER DISTILLATE
AP7 Sc
(SATURATE FRACTION)

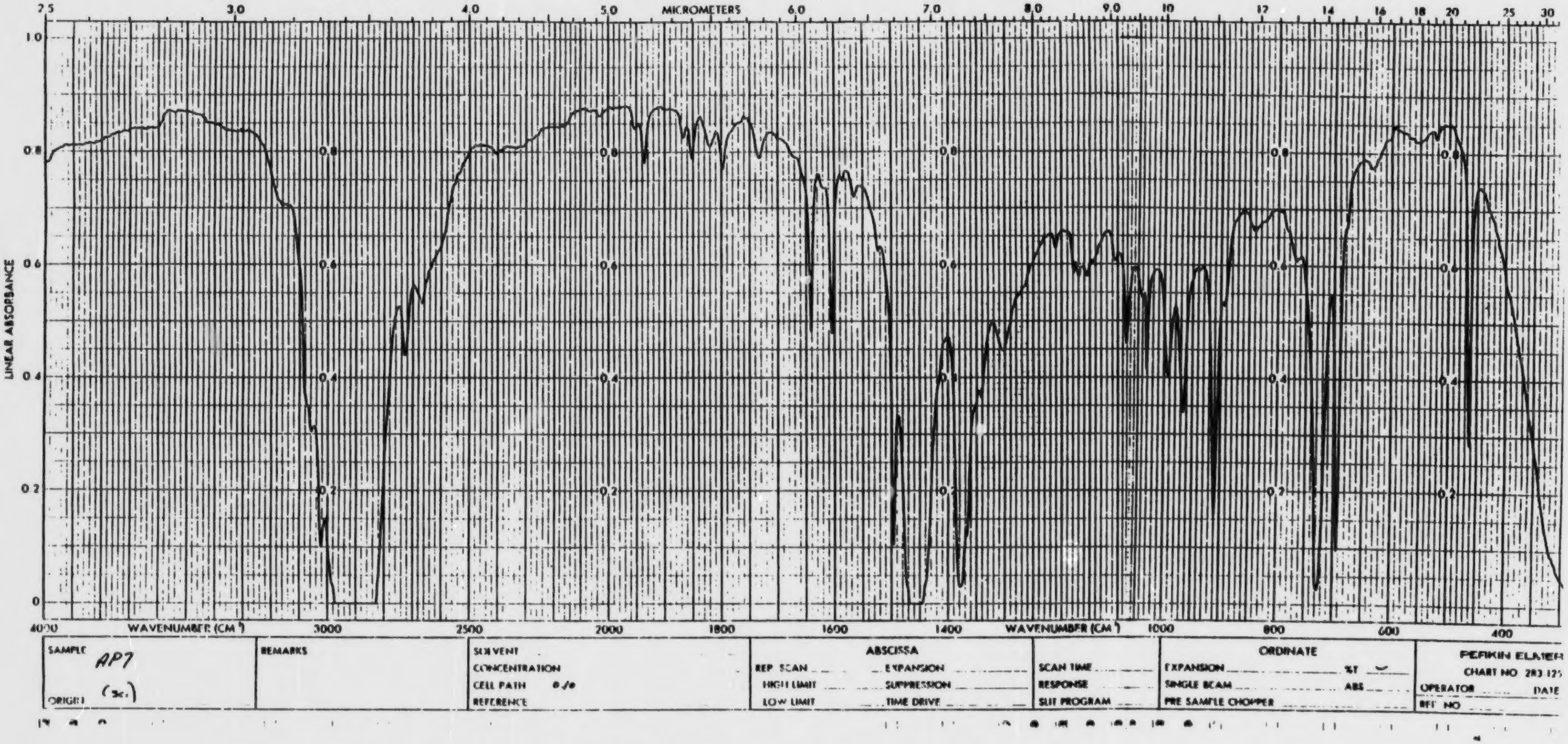
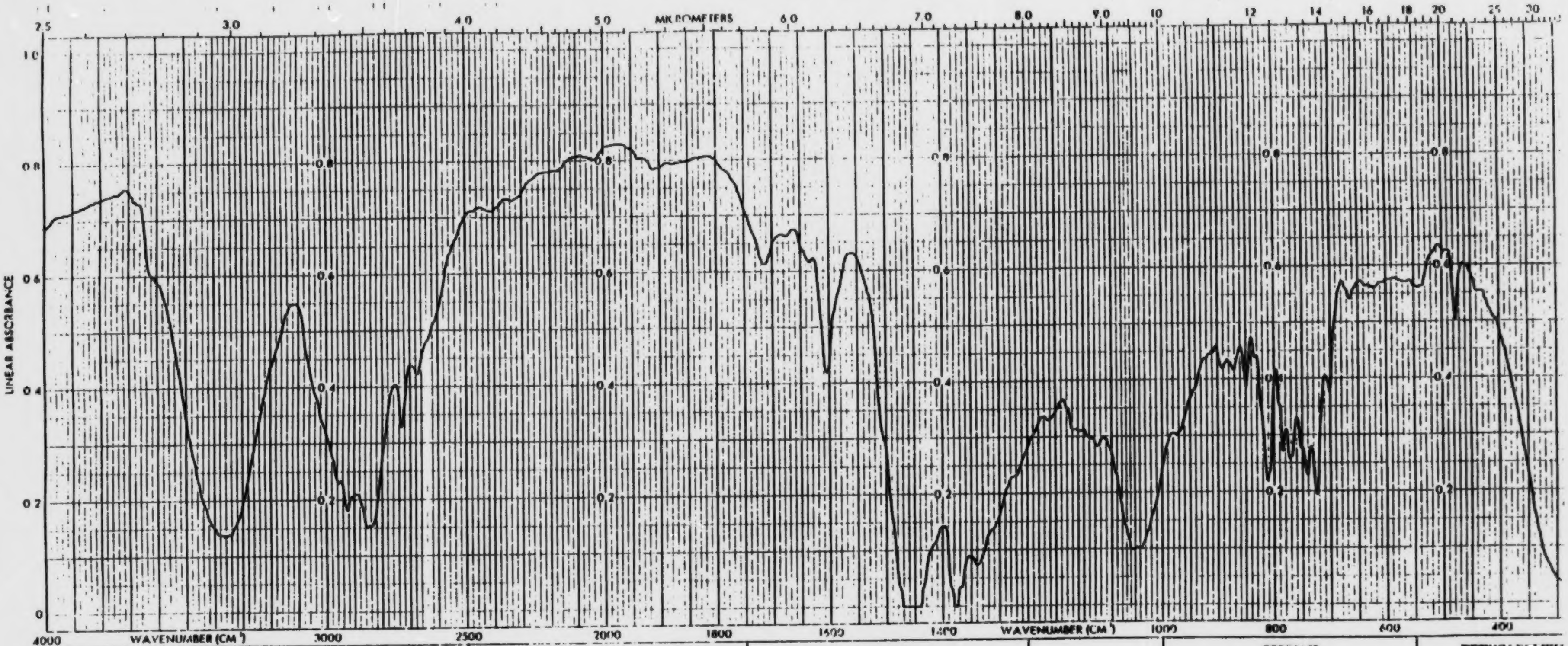


FIGURE 5,7F

EDMONTON COKER DISTILLATE
AP7 HB
(HYDROBORATED SAMPLE)



SAMPLE HB7B ✓ ORIGIN	REMARKS	SOLVENT CONCENTRATION CELL PATH 0.114 REFERENCE	ABSCISSA REF. SCAN ____ EXPANSION ____ HIGH LIMIT ____ SUPPRESSION ____ LOW LIMIT ____ TIME DRIVE ____	SCAN TIME ____ RESPONSE ____ SLIT PROGRAM ____	ORDINATE EXPANSION ____ %T ____ SINGLE BEAM ____ ABS ____ TPE SAMPLE CHOPPER ____

PERKIN ELMER
CHART NO. 283-125
OPERATOR ____ DATE
REF. NO.

5.8 Summary of Analytical Data for Physical Characteristics and Hydrocarbon Composition of Seven Middle Distillates

Methods expressed in Experimental Section 4 were assessed for the seven middle distillate samples to determine:

(1) if methods could handle samples from different origins having very different characteristics.

(2) possible method improvements needed for handling difficult samples.

These methods included:

(1) Physical Characterization Methods (Table 5.8A e.g. density, aniline point (D611), distillations (D86).

(2) Hydrocarbon Composition, e.g. LRMS, GCMS, NMR

5.8.1 Physical Characteristics of Middle Distillates

Standard Methods (ASTM, CGSB) characterized the physical properties of the seven middle distillates (Section 5.1-5.7) and are summarized in Table 5.8A. The origin of the distillate resulted in very different distillate physical characteristics. For example, the "standard" commercially available diesel fuel (AP5) had a density of 0.8205 g/cc compared to the high density of 0.9245 g/cc for the Syncrude EFV (AP6).

Boiling ranges, as reflected by density, also varied widely within the distillation limits of 160°C to 340°C.

Direct comparisons between distillates should be done with caution since the hydrocarbon composition of one boiling range should not be directly compared to distillates of a different boiling range. Therefore, to say one distillate is a better blending fuel than another distillate is erroneous unless a totally blended "commercial" fuel is evaluated. Trends, however, in diesel fuel quality can be determined.

The cetane indices (both ASTM and CGSB) gave similar results for most of the distillates except for the Wyodak Liquified Coal (AP4) and Syncrude EFV (AP6). The matrix upon which these cetane indices were founded was different from the middle distillates tested and therefore the results calculated do not necessarily reflect engine performance.

As expected, the commercial diesel (AP5) had the physical characteristics (cetane index, density, boiling range) necessary for selling a diesel fuel while the other distillates did not meet the commercial specifications. Since the six of the seven distillates varied extensively from the commercial diesel, the hydrocarbon composition was characterized (paraffins, aromatics, olefins) to determine how the inadequate diesel quality was related to hydrocarbon composition.

5.8.2 Distillate Hydrocarbon Composition

As illustrated in Sections 5.1 to 5.7, various methods were used to determine the distillate hydrocarbon compositions (Table 5.8B). These methods included:

Saturate Fraction 1. Paraffins 2. Cycloparaffins	]	Liquid chromatography Separation LRMS GCMS
Aromatic Fraction	]	Liquid Chromatography Separation LRMS GCMS NMR
Resins	-	Liquid Chromatography Separation
Olefins	]	Hydroboration - I.R. - GCMS (TNS Ether) Bromine Number NMR
N-Paraffin Content of Separation Saturate Fraction	]	GC GCMS

TABLE 5.8A

Summary Table of Distillate Physical Characteristics

	AP1 Suncor Coker Kerosene	AP2 Suncor Hydrotreated LGO	AP3 Husky Fireflood Oil	AP4 Wyodak Liquified Coal	AP5 Commercial Diesel MR5-10-1	AP6 Syncrude EFV O/H	AP7 Edmonton Coker Distillate
Density @ 15°C (g/cc)	0.8800	0.8381	0.8876	0.8734	0.8205	0.9245	0.8295
Aniline Point °C (ASTM D611)	39.8	59.0	54.6	28.5	58.1	37.6	48.5
Viscosity @ 40°C (ASTM D445)	2.53	2.20	4.2	1.67	1.54	6.75	1.57
Distillation, (ASTM D86)							
IBP	195	205	207	176	166	252	162
10	229	215	237	180	187	276	193
20	238	219	253	189		286	203
30	243	223	268	191		293	210
40	246	228	280	195		299	217
50	251	232	290	200	220	305	224
60	255	236	299	208		311	231
70	260	241	*	214		318	239
80	266	248	*	221		325	247
90	275	258	*	236	268	333	257
FBP	296	290	*	257	303	346	277
Cetane Index (ASTM D976)	34.4	42.1	40.5	19.2	44.3	34.1	42.4
Cetane Index (CGSB)	31.6	43.0	--	27.3	43.2	27.9	37.2

*The sample foamed during D86.

5.8.2A Hydrocarbon Composition by LRMS and GCMS

As illustrated in Table 5.8B, the total saturate composition (paraffins and cycloparaffins) as well as aromatics determined by LRMS and GCMS agreed to within 6 wt.% for most samples except for Suncor coker kerosene (AP1), Husky Fireflood (AP3) distillate and Syncrude EFV O/H (AP6). Since the agreement in paraffin content for all samples is excellent between LRMS and GCMS, the discrepancies were due to the matrix differences for classifying cycloparaffins and aromatics. In all seven samples, the GCMS cycloparaffin concentrations were higher than the LRMS analyses (Table 5.8C) while the reverse was true with aromatics. These total saturate discrepancies were seen the worst in samples containing the highest aromatic concentrations (AP1, AP3 and AP8).

TABLE 5.8B

Summary Table of Distillate Hydrocarbon Composition

		AP1 Suncor Coker Kerosene	AP2 Suncor Hydrotreated LGO	AP3 Husky Fireflood	AP4 Wyodak Liquified Coal	AP5 Commercial Diesel	AP6 Syncrude EFV O/H	AP7 Edmonton Coker
Hydrocarbon Composition								
Saturates (Total)	Separation	(60)	(75)	(64)	(62)	(74)	(44)	(66)
	LRMS	67	79	68	78	77	50	73
	GCMS	74	84	76	81	83	63	79
Paraffins	Separation	(13)	(25)	(12)	(3)	(39)	(3)	(31)
	LRMS	13	26	10	2	40	2	33
	GCMS	14	26	13	2	42	4	39
n-paraffin	GC	1	3	0.1	0.1	9	0.1	8
	GCMS	1	3	0.3	0.1	10	0.1	9
Cycloparaffins	Separation	(47)	(50)	(52)	(59)	(35)	(41)	(35)
	LRMS	54	53	58	76	37	48	40
	GCMS	60	58	63	79	41	59	40
Aromatics	Separation	(32)	(20)	(31)	(24)	(22)	(45)	(27)
	LRMS	33	21	32	22	23	50	27
	GCMS	26	16	24	19	17	37	21
	NMR	6	4	3	7	4	7	4
Resins		(8)	(5)	(5)	(14)	(4)	(11)	(7)
Olefins	I.R. wt.% O.H.	10	0	0	14	0	6	13
	GCMS wt.% by TMS Ether	34	0	0	13	0	20	38
	Wt. % by Bromine No.	38	0	10	13	0	25	41
	Wt. % by NMR	5.5	4.3	3.4	6.8	4.4	7.1	4.5

( ) Back calculated from LRMS on saturate fraction.

5.8.2B Hydrocarbon Composition by Liquid Chromatography followed by LRMS and Recalculation

Samples separated into the three components (saturates, aromatics, resins) by liquid chromatography (Section 4.2) agreed well with LRMS and GCMS results. Resin data obtained from the liquid chromatographic procedure was categorized as cycloparaffins when comparing the three procedures (Table 5.8D). Agreements between the three methods (Separation, LRMS and GCMS) were very good with liquid separation data closely matching the LRMS to within 2 wt.% in all distillates except the Syncrude EFV (O/H) which agreed to within 5 wt.%

TABLE 5.8C

Summary Table of LRMS and GCMS Data

Percent Difference

		AP1	AP2	AP3	AP4	AP5	AP6	AP7
Saturates (Total)	LRMS-GCMS	-7	-5	-8	-3	-5	-13	-6
Paraffins	LRMS-GCMS	-1	0	-3	0	-2	-2	-6
Cycloparaffins	LRMS-GCMS	-6	-5	-5	-3	-4	-11	0
Aromatics	LRMS-GCMS	+7	+5	+8	+3	+5	+13	+6

TABLE 5.8D

Summary Table of Liquid Chromatography Separation Recalculations, LRMS and GCMS Data

	AP1	AP2	AP3	AP4	AP5	AP6	AP7
Saturates (Total)							
Separation (+ Resin)	(68)	(80)	(69)	(76)	(78)	(55)	(73)
LRMS	67	79	68	78	77	50	73
GCMS	74	84	76	81	83	63	79
Paraffins							
Separation	(13)	(25)	(12)	(3)	(39)	(3)	(31)
LRMS	13	26	10	2	40	2	33
GCMS	14	26	13	2	42	4	39
Cycloparaffins							
Separation (+ Resins)	(55)	(55)	(57)	(73)	(39)	(52)	(42)
LRMS	54	53	58	76	37	48	40
GCMS	60	58	63	79	41	59	40
Aromatics							
Separation	(32)	(20)	(31)	(24)	(22)	(45)	(27)
LRMS	33	21	32	22	23	50	27
GCMS	26	16	24	19	17	37	21

5.8.2C N-Paraffin Composition

Paraffins in the saturate fraction were divided into two categories:

1. Normal paraffins
2. Iso-Paraffins

GCMS and GC methods (Section 4.4 & 4.6) were used to determine the n-paraffin content of the saturate fraction. The molecular sieve adsorption method originally proposed was discarded due to inaccurate and inconsistent results for hydrocarbons beyond C_{13} (Appendix IIA). From the Tables 5.1D to 5.7D and Table 5.8D, the n-paraffin content by both GC and GCMS were very repeatable both in total n-paraffin content and n-paraffin distribution by carbon number. The samples with the highest n-paraffin and total paraffin content were Suncor Hydrotreated LGO (AP2), Commercial diesel (AP5) and Edmonton coker distillate (AP7) which had the highest cetane indices and lowest densities.

5.8.2D Olefin Determination

Three methods used to determine the olefin content (Table 5.8B) were:

1. Hydroboration followed by I.R. analyses of OH group (Section 4.5)
2. Hydroboration followed by converting the OH group to trimethyl silylate (TMS) using TMS reagent (Section 4.6.3)
3. Bromine Number

Problems encountered in the recovery (<85 wt%) of sample during the hydroboration method (N.A. Poirier and A.E. George, Fuels, 60 (1981) 194) were resolved (Appendix IIA) by controlling sample evaporation.

The I.R. determination (Section 4.5) of wt.% OH was only used as a guide to determine if olefins were or were not present in the different distillates. Exact calculations of olefin content from the alcohol determination were very inaccurate (e.g. AP1 = 112% olefins) probably due to the inability to make a standard alcohol sample similar to the many different distillates tested. Without the "standard " solution, OH sensitivity and therefore sample OH concentration could not be determined accurately.

The TMS ethers concentration (Section 4.6.3) by GCMS were equivalent to the olefin concentrations since the molar concentrations remained constant.

The GCMS and Bromine Number values for olefins were in good agreement for all samples except the Husky Fireflood material and it is not known at this time why the discrepancy existed. As indicated by I.R., no olefins were present in the Suncor Hydrotreated LGO (AP2) and the commercial diesel. Due to the severity of the coker process both Suncor coker kerosene and Edmonton coker distillate contained very high amounts of olefinic material.

5.8E 'H NMR Results

Middle distillates analysed by proton nuclear magnetic resonance gave results which were inconsistent with any of the previous test methods discussed. There were a number of problems associated with quantitative analysis by NMR (see references 2-4) which make the data in Table 5.8E inaccurate when compared with GCMS (GCMS can separate and identify individual compounds). The 'H spectra results in signal overlaps producing difficulty to accurately indentify and integrate resonances of a single component or a class of compounds. Evidence of this occurs in the 2-alkyl region which contains signals from alkyl substituents on aromatic and olefinic groups as well as from the iso-paraffin compounds.

Although not part of the contract, an attempt was made to alleviate the above problems by using carbon-13 NMR. There was still, however, an overwhelming number of aliphatic carbon resonances compressed in a 30-40 ppm range making analyses of the hydrocarbon composition very difficult.

TABLE 5.8E

TABLE 1. Relative Composition of middle distillate samples

Protons	AP1	AP2	AP3	AP4	AP5	AP6	AP7
Aromatic	5.5	4.3	3.4	6.8	4.4	7.1	4.5
Olefinic	2.0					0.7	2.5
α-Alkyl	26.1	22.2	23.8	35.8	14.5	23.0	24.5
CH_2	35.7	38.7	35.0	30.1	45.0	34.4	44.7
CH_3	30.7	34.8	37.8	27.3	36.1	34.8	23.8

	AP1(SC)	AP2(SC)	AP3(SC)	AP4(SC)	AP5(SC)	AP6(SC)	AP7(SC)
Aromatic	0.3	0.2	1.0			1.1	
Olefinic	1.9					1.1	2.4
Toluene CH_3				1.3	0.7		2.3
α-Alkyl	17.6	12.9	20.0	31.6	11.3	13.8	14.5
CH_2	40.1	44.4	39.0	34.5	50.4	39.9	50.2
CH_3	40.1	42.5	40.0	32.6	37.6	44.1	30.6

	HB1B	HB2B	HB3B	HB4B	HB5B	HB6B	HB7B
Aromatic	5.1	2.7	4.0	6.7	4.5	6.3	3.6
Olefinic							
EtOH CH_2	0.3			2.1		0.5	
Total Alcohol	0.7					0.7	1.0
α-Alkyl	20.8	19.5	22.8	37.2	14.9	27.3	18.4
CH_2	36.5	41.3	34.6	27.5	45.0	29.9	51.9
CH_3	36.9	36.5	38.6	26.5	35.6	35.3	31.1

CONCLUSIONS

Analytical Methods Evaluation

1. Analytical procedures used to determine distillate compositions (saturates and aromatics) were in very good agreement for most samples.

   Hydrocarbon separation by liquid chromatography agreed very well with Low Resolution Mass Spectrometry data and to a lesser extent with gas chromatography - mass spectrometry. The differences between LRMS and GCMS have been attributed to differences in the matrixes used in the calculations. In the GCMS analyses, the aromatic components represented a 20-30% of the composite samples (except Syncrude Distillate) and the low concentration of numerous aromatic isomers therefore hide below the overall TIC envelope.

   The aromatics content by GCMS was therefore lower than LRMS results.

2. The n-paraffin data of the saturate fraction by Gas Chromatography (GC) and Gas Chromatography Mass Spectrometry (GCMS) were in very good agreement. The method suggested originally in the contract for n-paraffin determination by molecular sieves (Appendix IIA) was not applicable to these higher boiling (>253°C) distillates.

3. Iso-paraffins of the saturate fraction were difficult to quantify due to interferences from other profile peaks.

4. The NMR results did not agree with any of the data from LRMS and GCMS due to its inability to analyse highly branched aliphatic aromatics as one compound.

5. Two of the methods (GCMS, Bromine Number) used to determine olefin content agreed very well with each other. The infrared method on the hydroborated sample gave inconsistent results with the other two methods and should be used only as an indicator of olefins present or absent in a middle distillate sample.

Sample Analyses

1. As expected, distillates (160°C to 340°C) varied on physical characteristics and hydrocarbon composition according to their origin (Table 5.8A, 5.8B).

2. Boiling ranges of the seven samples varied widely and therefore direct comparisons should be done with care.

3. Commercial diesel had the highest cetane index, lowest aromatics, widest boiling range and lowest density making it a "good" diesel with minimum or no knock in diesel engine performance.

4. Suncor Hydrotreated LGO (AP2), commercial diesel (AP5) and Edmonton coker distillate (AP7) had the highest paraffin content (and n-paraffin content), the lowest aromatics and the highest cetane indices (greater than 40) indicating minimum diesel engine knock. (The effect of high olefinic content of the Edmonton coker distillate on engine performance is not known.)

5. Suncor Hydrotreated LGO (AP1), Husky Fireflood (AP3) and commercial diesel did not contain olefins.

6. All other coker products and Wyodak liquified coal contained high olefin content.

RECOMMENDATIONS

1. Due to the variability in sample composition, direct comparisons of distillates should be done with caution when comparing ASTM procedures. For example, cetane index does not indicate engine performance for unconventional middle distillates but does indicate engine performance trends for conventional fuels (indices were created on conventional fuel parameters).

2. Further improvements on olefin methods should be made to confirm why, for example, the bromine number differed so drastically from the GCMS olefin determination of Husky Fireflood LGO (AP2). The olefin determination by infrared should be used only as an indication of olefins present or absent.

3. The molecular sieve method for n-paraffins in the distillate saturate fraction should not be used. Instead, GC and GCMS can identify the n-paraffin content and the associated carbon numbers.

4. Discrepancies between LRMS and GCMS should be resolved by adjusting hydrocarbon matrix to varying sample origins.

5. Proton NMR should be used with caution for hydrocarbon work. C_{13} in conjunction with 'H NMR would give more accurate results.[1]

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APPENDIX I

HYDROCARBON SEPARATION CALCULATIONS

Each middle distillate sample was separated into four hydrocarbon classifications by column chromatography. Of the four fractions, saturates and mono-diaromatic samples were analysed by low resolution mass spectrometry (LRMS). The compositon of each fraction from LRMS was then used to calculate the composition of the initial sample before separation. The amounts of polyaromatics and resin from the hydrocarbon separation procedure were not enough for mass spectrometry compositions and, for the calculations, were therefore assumed to be purely polyaromatics and purely resins without contamination by saturates and mono-diaromatics. The calculated normalized results from recombining the hydrocarbon fractions were compared to the low resolution mass spectrometer composition of the feed sample (as is). The calculations for each of the seven middle distillate samples are listed in Tables 1 to 7.

Each middle distillate was separated by column chromatography, a minimum of three times, using the AP60 hydrocarbon separation procedure. For example, Table 1 shows the data for Suncor Coker Kerosene (AP1). The numbers one to three along the top of the table show data for each of the three separations performed. The first column on the left (Feed M.S.) is the low resolution mass spectrometry compositional on a middle distillate sample (AP1) before separation.

The column tables "Sep." is the normalized weight percent of the four fractions after separation.

Saturates	63.0 wt.%
Mono-diaromatics	27.9 wt.%
Polynuclear aromatics	1.1 wt.%
Resins	8.0 wt.%
	100.0 wt.%

The third column, "1S", is the low resolution mass spectrometry composition for the saturate fraction (1st extraction). From Table 1, the sum of the saturate (59.3 wt.%) and aromatics (3.7 wt.%), composition is the total saturates recovered from the chromatographic separation (63.0 wt.%). Similarily, the fourth column, "1MA", is the low resolution mass spectrometry composition for the mon-diaromatic fraction (1st extraction). The sum of the saturates (1.5 wt.%) and aromatics (26.4 wt.%) is the total weight of mono-diaromatics recovered from the chromatographic separation (27.9 wt.%). The fifth column, "1S+ 1MA" is the sum of the two normalized fractions, saturates and mono-diaromatics. The sixth column, "Tot", is the normalized calculated composition of the recombined fractions.

The saturate samples combined for further work such as infrared, gas chromatography, gas chromatography - mass spectrometry and nuclear magnetic resonance is indicated at the bottom of the table (i.e. saturate fractions of all three (1,2 & 3) were combined).

TABLE 1

Normalized Mass Spectrometry Data for AP1 Suncor Coker Kerosine

Separation		1					2					3				
	Feed M.S.	Sep.	1S	1MA	1S+ 1MA	Tot.	Sep.	2S	2MA	2S+ 2MA	Tot.	Sep	3S	3MA	3S+ 3MA	Tot.
Hydrocarbon Types M.S. wt%																
Recovery (wt%)		97					97					92				
Saturates	67.3	63.0	59.3	1.5	60.8	60.8	60.3	56.7	1.2	57.9	57.9	62.7	59.9	1.3	61.2	61.2
Paraffins	12.6	-	13.1	0	13.1	13.1	-	12.6	0	12.6	12.6	-	13.2	0	13.2	13.2
Cycloparaffins	54.7	-	46.2	1.5	47.7	47.7	-	44.1	1.2	45.3	45.3	-	46.7	1.3	48.0	48.0
Aromatics	32.7	29.0	3.7	26.4	30.1	31.2	31.0	3.6	28.7	32.3	33.4	28.7	2.8	25.7	28.5	30.2
Monoaromatics	21.1	27.9	3.1	16.6	19.7	19.7	29.9	2.6	19.0	21.6	21.6	27.0	2.1	16.3	18.4	18.4
Diaromatics	6.2		0.1	4.9	5.0	5.0		0.6	4.9	5.5	5.5		0	4.8	4.8	4.8
Polynuclear	5.4	1.1	0.5	4.9	5.4	6.5	1.1	0.4	4.8	5.2	6.3	1.7	0.7	4.6	5.3	7.0
Resins	0	8.0	0	0	0	8.0	8.7	0	0	0	8.7	8.6	0	0	0	8.6

Feed M.S. = LRMS Feed Composition
1 = Separation No.
S = Mono-Diaromatics
Tot.= Calculated Composition

combined

APISC
1S+2S+3S

TABLE 2

Normalized Mass Spectrometry Data for AP2 Suncor HT

(No Ice)

Separation		1					2					3				
	Feed M.S.	Sep.	1S	1MA	1S+ 1MA	Tot.	Sep.	2S	2MA	2S+ 2MA	Tot.	Sep	3S	3MA	3S+ 3MA	Tot.
Hydrocarbon Types																
M.S. wt%																
Recovery (wt%)		88					92					95				
Saturates	79.1	77.3	77.1	0	77.1	77.1	76.9	72.9	0.4	73.3	73.3	76.4	75.7	0	75.7	75.7
Paraffins	26.3	-	25.9	0	25.9	25.9	-	24.7	0.1	24.8	24.8	-	26.3	0	26.3	26.3
Cycloparaffins	52.8	-	51.2	0	51.2	51.2	-	48.2	0.3	48.5	48.5	-	49.4	0	49.4	49.4
Aromatics	20.9	19.9	0.2	19.0	19.2	20.1	15.7	4.0	14.5	18.5	19.3	19.3	0.7	18.8	19.5	20.0
Monoaromatics	18.7	19.0	0	18.0	18.0	18.0	14.9	2.8	13.5	16.3	16.3	18.8	0.5	17.4	17.9	17.9
Diaromatics	2.2		0.2	1.0	1.2	1.2		1.1	1.0	2.1	2.1		0.2	1.4	1.6	1.6
Polynuclear	0	0.9	0	0	0	0.9	0.8	0.1	0	0.1	0.9	0.5	0	0	0	0.5
Resins	0	2.8	0	0	0	2.8	7.4	0	0	0	7.4	4.3	0	0	0	4.3

Feed M.S. = LRMS Feed Composition
1 = Separation No.
S = Mono-Diaromatics
Tot.= Calculated Composition

combined

AP2SC
1S+3S

TABLE 3

Normalized Mass Spectrometry Data for AP3 Husky Fireflood (160-340°C)

Separation		1					2					3				
	Feed M.S.	Sep.	1S	1MA	1S+ 1MA	Tot.	Sep.	2S	2MA	2S+ 2MA	Tot.	Sep	3S	3MA	3S+ 3MA	Tot.
Hydrocarbon Types M.S. wt%																
Recovery (wt%)		79					94					91				
Saturates	68.3	67.7	61.9	1.2	63.1	63.1	72.0	61.9	0	61.9	61.9	70.1	66.1	0	66.1	66.1
Paraffins	9.6	-	11.0	0.1	11.1	11.1	-	10.6	0	10.6	10.6	-	13.6	0	13.6	13.6
Cycloparaffins	58.7	-	50.9	1.1	52.0	52.0	-	51.3	0	51.3	51.3	-	52.5	0	52.5	52.5
Aromatics	31.7	25.8	5.8	23.5	29.3	30.4	21.4	10.1	17.0	27.1	31.5	28.5	4.0	23.8	27.8	32.5
Monoaromatics	18.3	24.7	3.2	14.7	17.9	17.9	17.0	8.9	9.6	18.5	18.5	23.8	2.9	15.1	18.0	18.0
Diaromatics	8.6		1.0	6.7	7.7	7.7	-	0.2	5.7	5.9	5.9	-	0.1	6.4	6.5	6.5
Polynuclear	4.8	1.1	1.6	2.1	3.7	4.8	4.4	1.0	1.7	2.7	7.1	4.7	1.0	2.3	3.3	8.0
Resins	0	6.5	0	0	0	6.5	6.6	0	0	0	6.6	1.4	0	0	0	1.4

Feed M.S. = LRMS Feed Composition
1 = Separation No.
S = Mono-Diaromatics
Tot.= Calculated Composition

combined

AP3SC
2S+3S

TABLE 4

Normalized Mass Spectrometry Data for AP4 Wyodak Liquified Coal (160°C+)

Separation		4					5					7				
	Feed M.S.	Sep.	4S	4MA	4S+ 4MA	Tot.	Sep.	5S	5MA	5S+ 5MA	Tot.	Sep	7S	7MA	7S+ 7MA	Tot.
Hydrocarbon Types																
M.S. wt%																
Recovery (wt%)		99					97					93				
Saturates	78.4	61.7	58.3	0	58.3	58.3	70.3	65.0	0	65.0	65.0	70.0	63.3	0	63.3	63.3
Paraffins	2.0	-	3.0	0	3.0	3.0	-	3.3	0	3.3	3.3	-	4.7	0	4.7	4.7
Cycloparaffins	76.4	-	55.3	0	55.3	55.3	-	61.7	0	61.7	61.7	-	58.6	0	58.6	58.6
Aromatics	21.6	21.2	3.4	20.7	24.1	24.6	17.6	5.3	16.8	22.1	22.9	12.2	6.7	11.2	17.9	18.9
Monoaromatics	19.9	20.7	3.3	20.4	23.7	23.7	16.8	5.3	16.1	21.4	21.4	11.2	6.7	10.6	17.3	17.3
Diaromatics	1.7		0.1	0.3	0.4	0.4		0	0.7	0.7	0.7		0	0.6	0.6	0.6
Polynuclear	0	0.5	0	0	0	0.5	0.8	0	0	0	0.8	1.0	0	0	0	1.0
Resins	0	17.1	0	0	0	17.1	12.1	0	0	0	12.1	17.8	0	0	0	17.8

Feed M.S. = LRMS Feed Composition
1 = Separation No.
S = Mono-Diaromatics
Tot.= Calculated Composition

combine

AP4SC
4S+5S

TABLE 5

Normalized Mass Spectrometry Data for AP5 Commercial Diesel
(MRS-10-11)

Separation		4					6					7				
	Feed				4S+					6S+					7S+	
	M.S.	Sep.	4S	4MA	4MA	Tot.	Sep.	6S	6MA	6MA	Tot.	Sep	7S	7MA	7MA	Tot.
Hydrocarbon Types M.S. wt%																
Recovery (wt%)		88					92					96				
Saturates	77.3	79.6	77.5	0	77.5	77.5	76.9	73.3	0	73.3	73.3	73.6	70.1	0	70.1	70.1
Paraffins	40.0	-	41.0	0	41.0	41.0	-	38.4	0	38.4	38.4	-	36.6	0	36.6	36.6
Cycloparaffins	37.3	-	36.5	0	36.5	36.5	-	34.9	0	34.9	34.9	-	33.5	0	33.5	33.5
Aromatics	22.7	17.1	2.1	15.6	17.7	19.2	19.9	3.6	18.3	21.9	23.5	19.6	3.5	17.9	21.4	23.1
Monoaromatics	18.5	15.6	1.7	11.4	13.1	13.1	18.3	3.2	14.0	17.2	17.2	17.9	3.0	13.8	16.8	16.8
Diaromatics	4.0		0.4	4.0	4.4	4.4		0.4	4.2	4.6	4.6		0.4	4.1	4.5	4.5
Polynuclear	0.2	1.5	0	0.2	0.2	1.7	1.6	0	0.1	0.1	1.7	1.7	0.1	0	0.1	1.8
Resins	0	3.3	0	0	0	3.3	3.2	0	0	0	3.2	6.8	0	0	0	6.8

Feed M.S. = LRMS Feed Composition
1 = Separation No.
S = Mono-Diaromatics
Tot.= Calculated Composition

combined

AP5SC
4S+6S+7S

TABLE 6

Normalized Mass Spectrometry Data for AP6 Syncrude EFV O/H

Separation		1					2					3				
	Feed				1S+					2S+					3S+	
	M.S.	Sep.	1S	1MA	1MA	Tot.	Sep.	2S	2MA	2MA	Tot.	Sep	3S	3MA	3MA	Tot.
Hydrocarbon Types																
M.S. wt%																
Recovery (wt%)		99					100					97				
Saturates	50.1	50.9	44.0	0	44.0	44.0	53.7	44.2	0	44.2	44.2	52.5	44.4	0	44.4	44.4
Paraffins	2.1	-	3.3	0	3.3	3.3	-	3.0	0	3.0	3.0	-	3.4	0	3.4	3.4
Cycloparaffins	48.0	-	40.7	0	40.7	40.7	-	41.2	0	41.2	41.2	-	41.0	0	41.0	41.0
Aromatics	49.9	38.5	6.9	31.8	38.7	45.4	34.8	9.5	28.0	37.5	44.3	36.9	8.1	29.8	37.9	45.0
Monoaromatics	23.8	31.8	3.7	17.0	20.7	20.7	28.0	6.1	14.1	20.2	20.2	29.8	5.4	15.5	20.9	20.9
Diaromatics	14.4		0.9	9.3	10.2	10.2		0.9	8.8	9.7	9.7		0.9	9.2	10.1	10.1
Polynuclear	11.7	6.7	2.3	5.5	7.8	14.5	6.8	2.5	5.1	7.6	14.4	7.1	1.8	5.1	6.9	14.0
Resins	0	10.6	0	0	0	10.6	11.5	0	0	0	11.5	10.6	0	0	0	10.6

Feed M.S. = LRMS Feed Composition
1 = Separation No.
S = Mono-Diaromatics
Tot.= Calculated Composition

Combined

AP6SC
1S+2S+3S

TABLE 7

Normalized Mass Spectrometry Data for AP7 Edmonton Coker Distillate

Separation		3					4					5				
	Feed M.S.	Sep.	3S	3MA	3S+ 3MA	Tot.	Sep.	4S	4MA	4S+ 4MA	Tot.	Sep	5S	5MA	5S+ 5MA	Tot.
Hydrocarbon Types																
M.S. wt%																
Recovery (wt%)		97					99					99				
Saturates	73.2	78.9	66.1	0	66.1	66.1	72.4	63.7	0	63.7	63.7	77.8	68.0	0.1	68.1	68.1
Paraffins	32.9	-	31.3	0	31.3	31.3	-	29.4	0	29.4	29.4	-	31.6	0.1	31.7	31.7
Cycloparaffins	40.3	-	34.8	0	34.8	34.8	-	34.3	0	34.3	34.3	-	36.4	0	36.4	36.4
Aromatics	26.8	16.2	12.8	14.4	27.2	29.0	18.8	8.7	18.3	27.0	27.0	16.5	9.8	16.0	25.8	26.2
Monoaromatics	22.0	14.4	12.4	10.3	22.7	22.7	18.3	8.2	14.2	22.4	22.4	16.1	9.4	11.7	21.1	21.1
Diaromatics	4.5		0.4	3.4	3.8	3.8		0.4	3.6	4.0	4.0		0.4	3.6	4.0	4.0
Polynuclear	0.3	1.8	0	0.7	0.7	2.5	0.5	0.1	0.5	0.6	1.1	0.4	0	0.7	0.7	1.1
Resins	0	4.9	0	0	0	4.9	8.8	0	0	0	8.8	5.7	0	0	0	5.7

Feed M.S. = LRMS Feed Composition
1 = Separation No.
S = Mono-Diaromatics
Tot.= Calculated Composition

Combined

AP7SC

3S+4S+5S

APPENDIX IIA

PROBLEMS ENCOUNTERED WITH METHODS

1. Hydrocarbon-type Separation

Seven middle distillate fractions were separated into saturates, mono-diaromatics, polynuclear aromatics and polar compounds using a dual silica-alumina column (modified API 60 method from CANMET by M.A. Pourier).

The following problems were found with this method:

a) Sample recovery on the lighter distillate fractions (e.g. 160-250°C) was very poor (69 to 85% vol.%). Loss of light ends during room temperature rotoevaporation was thought to be the problem. An ice bath during saturate evaporation was suggested to reduce light ends losses.

b) Complete separation between saturates and aromatics did not exist in some samples. Fractions of aromatics remain in the saturated fraction while some saturates remained in the aromatic fractions (Appendix I).

2. Olefin Determination

Seven middle distillate fractions were to be hydroborated according to a known procedure (M.A. Pourier and A.E. George, Fuels, 60 (1981) 194). This procedure is a gravimetric determination of olefins converted to alcohols and requires the weight of the final hydroborated sample to be larger than the initial sample weight. However, shown in Table 1, the hydroborated alcohol sample is not greater than the initial sample weight due to light ends loss. A rotary evaporator or heat was not used to evaporate the samples, instead they were air evaporated in a fumehood. This confirms the statement made in the method that "The procedure is not applicable to hydrocarbon mixtures in the boiling ranges lower than 200°C".

3. Determination of the n-Paraffin Content

Two of the seven fractions obtained from the hydrocarbon-type separation were analyzed for their n-paraffinic content using a molecular sieve adsorption method (Sista, V.R. and Srivastava, G.C., Analytical Chem. 48 (1976) 1582). The procedure claims that n-paraffin free C_{12}-C_{32} hydrocarbons adsorbed on 5A molecular sieves can be desorbed and removed from the U-shaped tube (designed by Nelson et al., Anal. Chem. 29 (1957) 1027) by heating the molecular sieves to 312°C at 0.5 mm Hg.

Approximate Boiling Points (°C)

	at 760 mm Hg	at 0.5 mm Hg
C_{12}	215	40
C_{32}	465	232
C_{49}	560	312

We found that the U-tube designed by Nelson et al. would not permit the escape of hydrocarbons beyond about C_{13}. This could have been due to condensation in the upper unheated regions of the U-tube near the ground-glass joints. The fraction that did escape the U-tube was collected in a cold trap and analyzed by high resolution capillary gas chromatography (Hewlett-Packard Application AN 228-34 and B.T. Hine, Chromatographics 18 (1984) 679). This is a much simpler procedure to test the total saturate fractions than the Sista and Sravastava procedure and we revised the procedure by using the high resolution capillary gas chromatography.

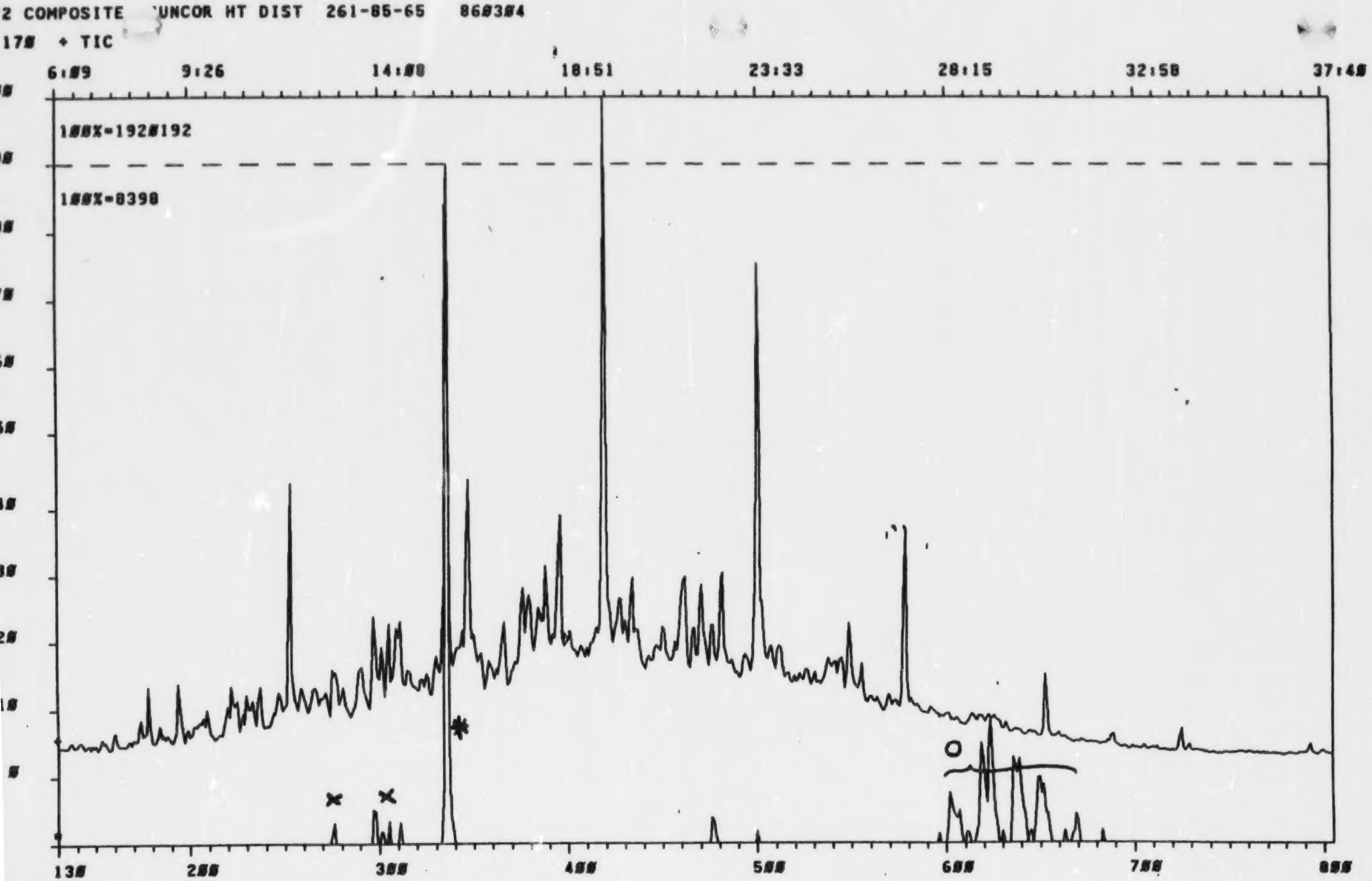
APPENDIX IIB

MOLECULAR ION TRACES OF COMPOSITE SAMPLES

The first two figures are examples of interpretation of the molecular ion traces and show the carbon number distributions of the various component types such as:

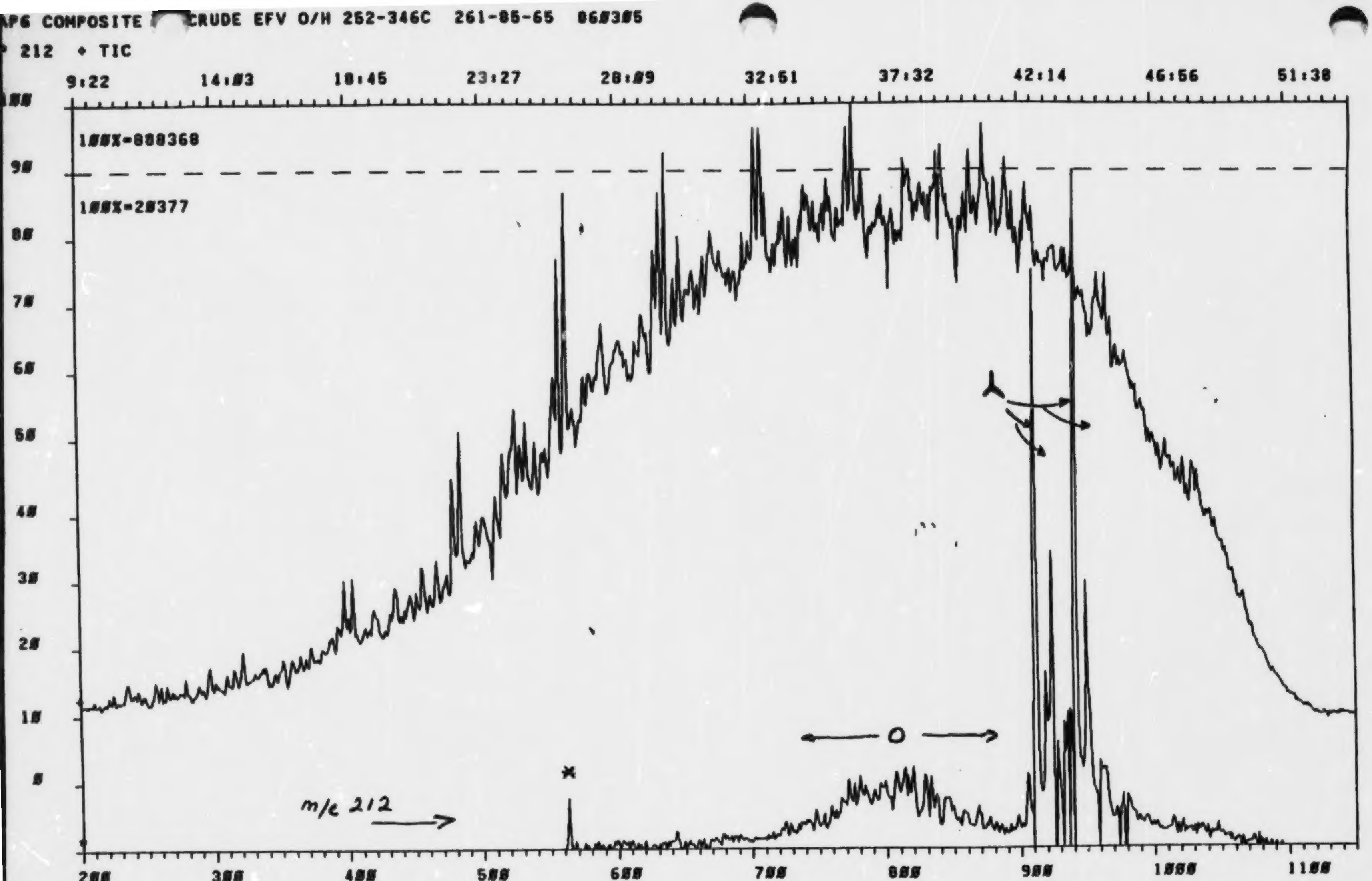
Z+2 paraffins
Z-6 alkyl benzene
Z-12 alkyl naphthalenes

The Husky Fireflood distillate showed few molecular ion trace features except Z-12 (alkyl-naphthalene). The lack of molecular ion features suggested that most substituents of the aromatic nucleus are highly branched much like the predominantly branched paraffin content of the sample.



Example of interpretation : m/e 170 , paraffins and alkylnaphthalenes

legend: × (iso) paraffins
* (n) paraffin
O alkyl naphthal.



Example of interpretation

m/e 212, Hydrocarbon types z+2 (paraffins) & z-12 (alkylnaphthal.) &
z-16S (alk. dibenzo thiophenes)

legend: * (n) paraffin, z+2
O [illegible]yl naphthalenes, z-12
[illegible] z-16S

(Backgnd corrected)

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                    GULF CANADA RESEARCH AND DEVELOPMENT DEPARTMENT

SAMPLE AP1 COMP.         SUNCOR COKER KEROSENE            ANALYSED: 1986 MAR  11.   13:41
PROJECT NO 261-85                                  RUN NUMBER F1052A             METHOD DIST

                  DISTILLATE ANALYSIS BY LOW RESOLUTION MASS SPECTROMETRY

                                                       DETERMINED             CALCULATED
    HYDROCARBON TYPE (CN.H2N-Z)     Z NO             VOLUME PERCENT          MASS PERCENT
    SATURATES                                                 76.36                  74.23
      PARAFFINS                      +2               16.24                  14.36
      CYCLOPARAFFINS                                       60.12                  59.87
        NONCOND CYCLOPARAFFINS        0               25.29                  23.83
        COND DICYCLOPARAFFINS        -2               21.38                  21.64
        COND POLYCYCLOPARAFFINS      -4               13.45                  14.40
    AROMATICS                                                 23.49                  25.77
      MONOAROMATICS                                        17.47                  18.32
        ALKYLBENZENES                -6                8.49                   8.49
        BENZOCYCLOPARAFFINS          -8                4.92                   5.39
        BENZODICYCLOPARAFFINS       -10                4.06                   4.44
      DIAROMATICS                                           3.30                   3.89
        NAPHTHALENES                -12                2.94                   3.42
        NAPHTHOCYCLOPARAFFINS       -14                0.00                   0.00
        FLUORENES                   -16                0.36                   0.47
      TRIAROMATICS                                          0.00                   0.00
        PHENANTHRENES/ANTHRACENE    -18                0.00                   0.00
        PHENANTHROCYCLOPARAFFINS    -20                0.00                   0.00
      TETRAAROMATICS                                        0.00                   0.00
        PYRENES/BENZOFLUORENES      -22                0.00                   0.00
        CHRYSENES/BENZANTHRACENE    -24                0.00                   0.00
      PENTAAROMATICS                                        0.00                   0.00
        CHRYSOCYCLOPARAFFINS        -26                0.00                   0.00
        BENZPYRENES/PERYLENES       -28                0.00                   0.00
        DIBENZANTHRACENES           -30                0.00                   0.00
      UNIDENTIFIED                                          0.00                   0.00
        Cn.H2n-32                   -32                0.00                   0.00
        Cn.H2n-36/Cn.H2n-26.S       -36                0.00                   0.00
        Cn.H2n-38/Cn.H2n-28.S       -38                0.00                   0.00
        Cn.H2n-42/Cn.H2n-32.S       -42                0.00                   0.00
        Cn.H2n-44/Cn.H2n-34.S       -44                0.00                   0.00
      AROMATIC SULFUR                                       2.71                   3.56
        BENZOTHIOPHENES             -10S               2.71                   3.56
        DIBENZOTHIOPHENES           -16S               0.00                   0.00
        BENZONAPHTHOTHIOPHENES      -22S               0.00                   0.00
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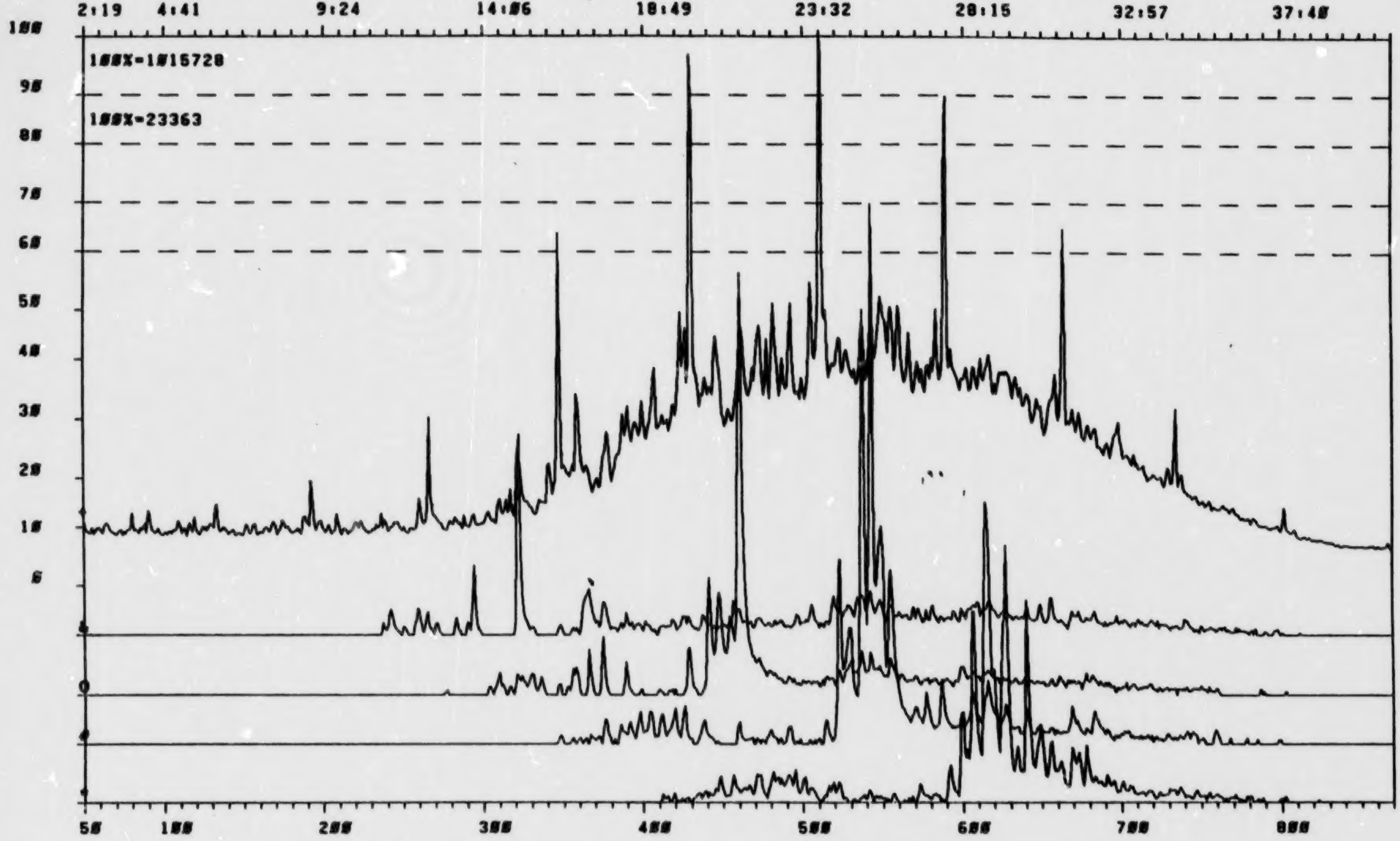
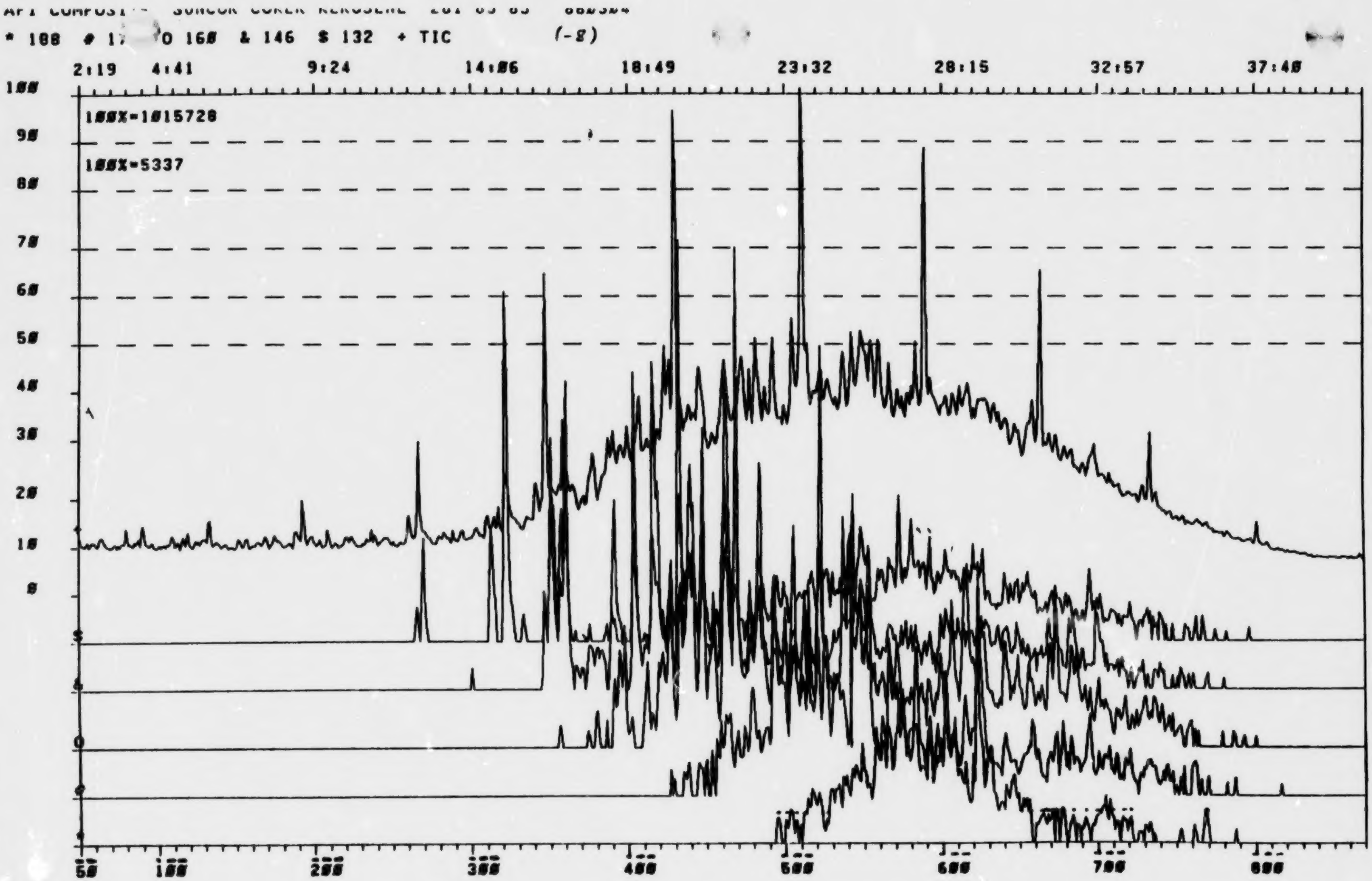
API COMPOSI SUNCOR COKER KEROSENE 261-85-65 860304

* 176 # 1 O 148 & 134 + TIC (-6, -10S)

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700
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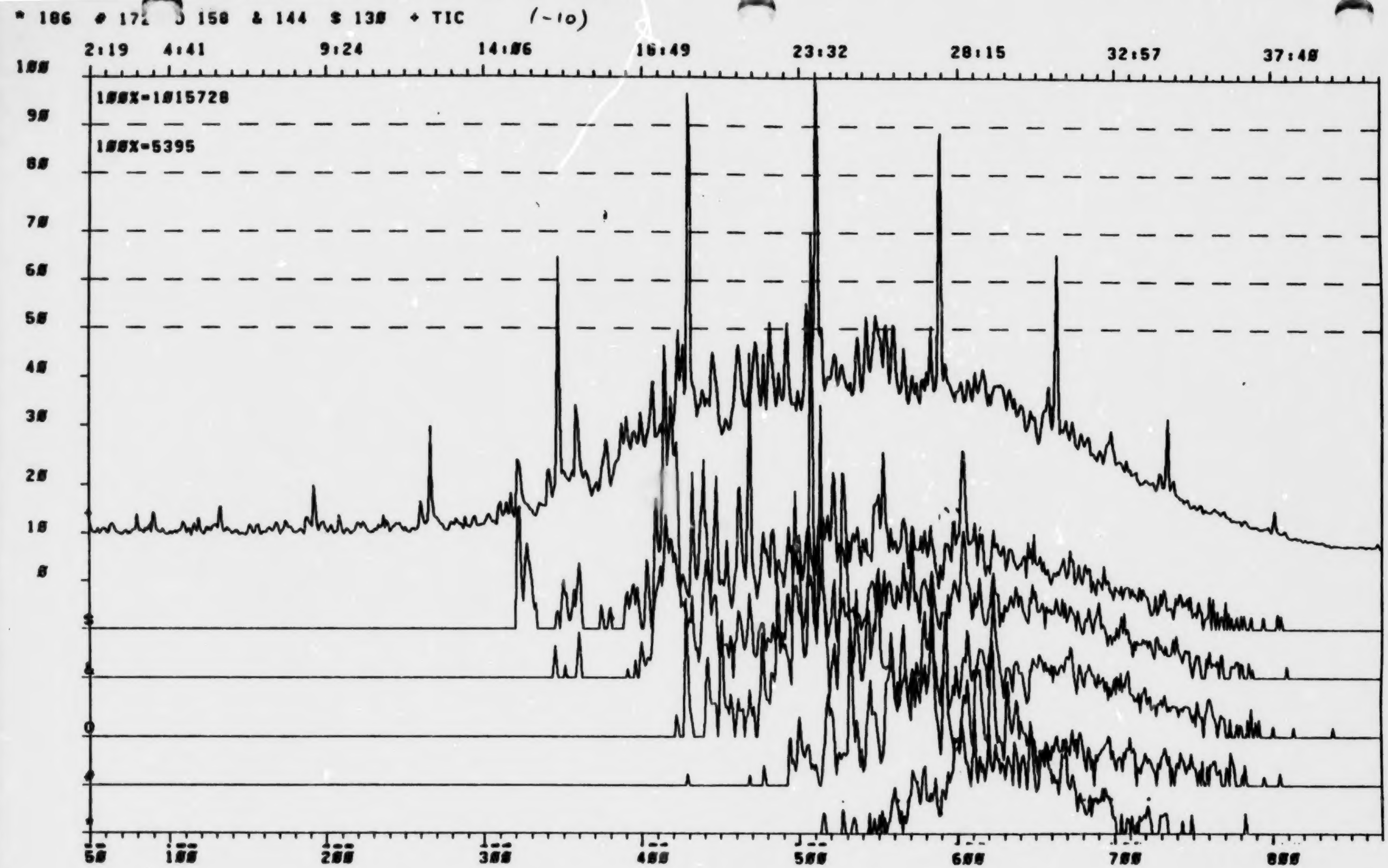
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(~10)
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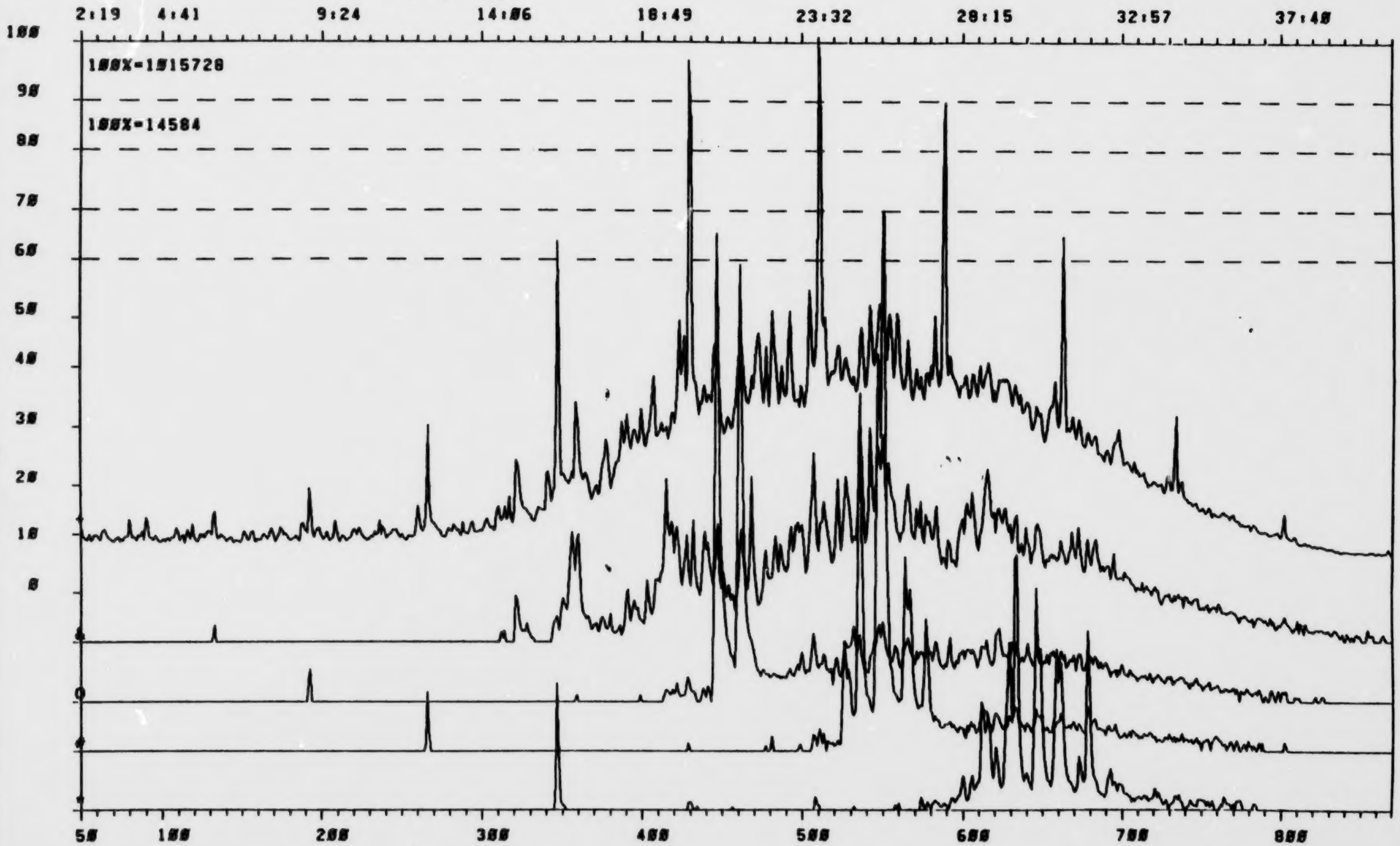
60
50
40
30
20
10
0
50
100
200
300
400
500
600
700
800

API COMPOSIT SUNCOR COKER KEROSENE 261-85-65 860304

* 170 # 156 O 142 & 128 + TIC (+2, -12)



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                     GULF CANADA RESEARCH [illegible]D DEVELOPMENT DEPARTMENT

SAMPLE AP2 COMP.             SUNCOR HT DIST                        ANALYSED: 1986 MAR  1[illegible].   14: 9
PROJECT NO 261-85                                    RUN NUMBER F1049A                   METHOD DIST

                      DISTILLATE ANALYSIS BY LOW RESOLUTION MASS SPECTROMETRY

                                                           DETERMINED              CALCULATED
   HYDROCARBON TYPE (CN.H2N-Z)       Z NO                VOLUME PERCENT           MASS PERCENT
   SATURATES                                                         84.86                   83.77
       PARAFFINS                      +2                27.87                   25.63
     CYCLOPARAFFINS                                           56.98                   58.13
       NONCOND CYCLOPARAFFINS          0                29.31                   28.73
       COND DICYCLOPARAFFINS          -2                23.20                   24.43
       COND POLYCYCLOPARAFFINS        -4                 4.47                    4.98
   AROMATICS                                                         14.86                   16.23
     MONOAROMATICS                                            13.92                   15.10
       ALKYLBENZENES                  -6                 7.55                    7.85
       BENZOCYCLOPARAFFINS            -8                 5.42                    6.16
       BENZODICYCLOPARAFFINS         -10                 0.95                    1.08
     DIAROMATICS                                               0.94                    1.14
       NAPHTHALENES                  -12                 0.94                    1.14
       NAPHTHOCYCLOPARAFFINS         -14                 0.00                    0.00
       FLUORENES                     -16                 0.00                    0.00
     TRIAROMATICS                                              0.00                    0.00
       PHENANTHRENES/ANTHRACENE      -18                 0.00                    0.00
       PHENANTHROCYCLOPARAFFINS      -20                 0.00                    0.00
     TETRAAROMATICS                                            0.00                    0.00
       PYRENES/BENZOFLUORENES        -22                 0.00                    0.00
       CHRYSENES/BENZANTHRACENE      -24                 0.00                    0.00
     PENTAAROMATICS                                            0.00                    0.00
       CHRYSOCYCLOPARAFFINS          -26                 0.00                    0.00
       BENZPYRENES/PERYLENES         -28                 0.00                    0.00
       DIBENZANTHRACENES             -30                 0.00                    0.00
     UNIDENTIFIED                                              0.00                    0.00
       Cn.H2n-32                     -32                 0.00                    0.00
       Cn.H2n-36/Cn.H2n-26.S         -36                 0.00                    0.00
       Cn.H2n-38/Cn.H2n-28.S         -38                 0.00                    0.00
       Cn.H2n-42/Cn.H2n-32.S         -42                 0.00                    0.00
       Cn.H2n-44/Cn.H2n-34.S         -44                 0.00                    0.00
     AROMATIC SULFUR                                           0.00                    0.00
       BENZOTHIOPHENES               -10S                0.00                    0.00
       DIBENZOTHIOPHENES             -16S                0.00                    0.00
       BENZONAPHTHOTHIOPHENES        -22S                0.00                    0.00
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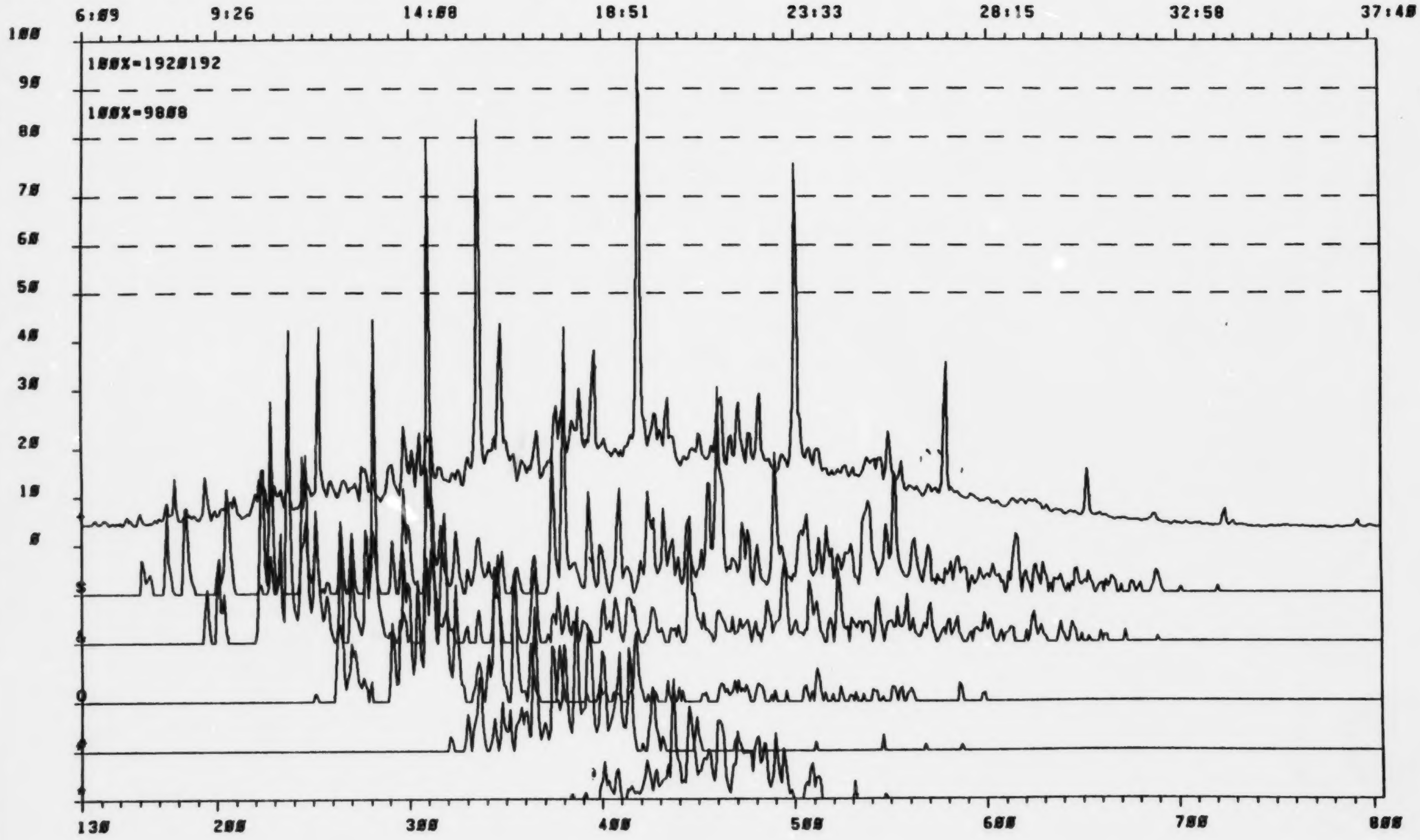
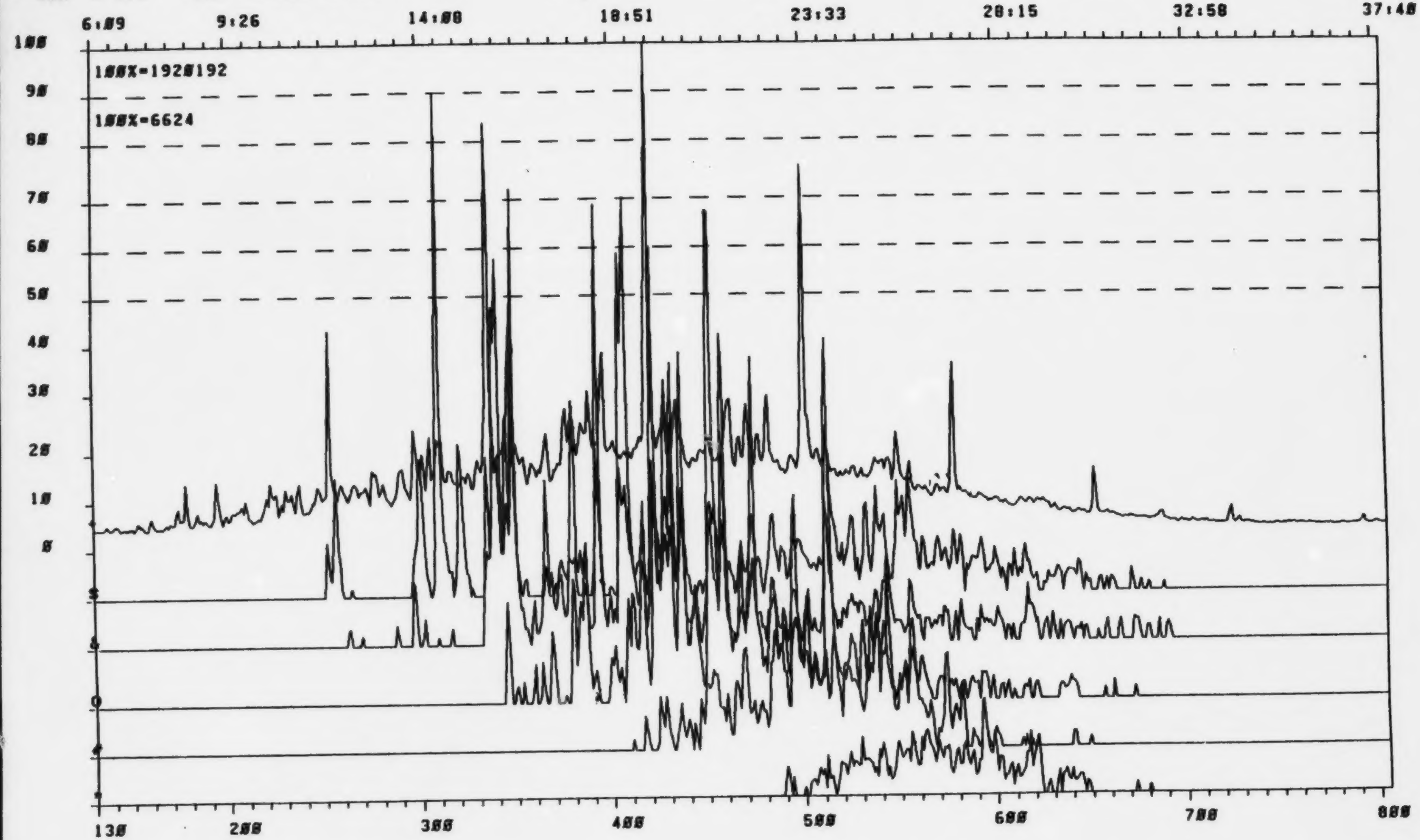
DS-55 CROSS SCAN REPORT, RUN: SP1045

AP2 COMPOSI SUNCOR HT DIST 261-85-65 860304

* 176 # 162 O 148 & 134 $ 120 + TIC (-6, -105)

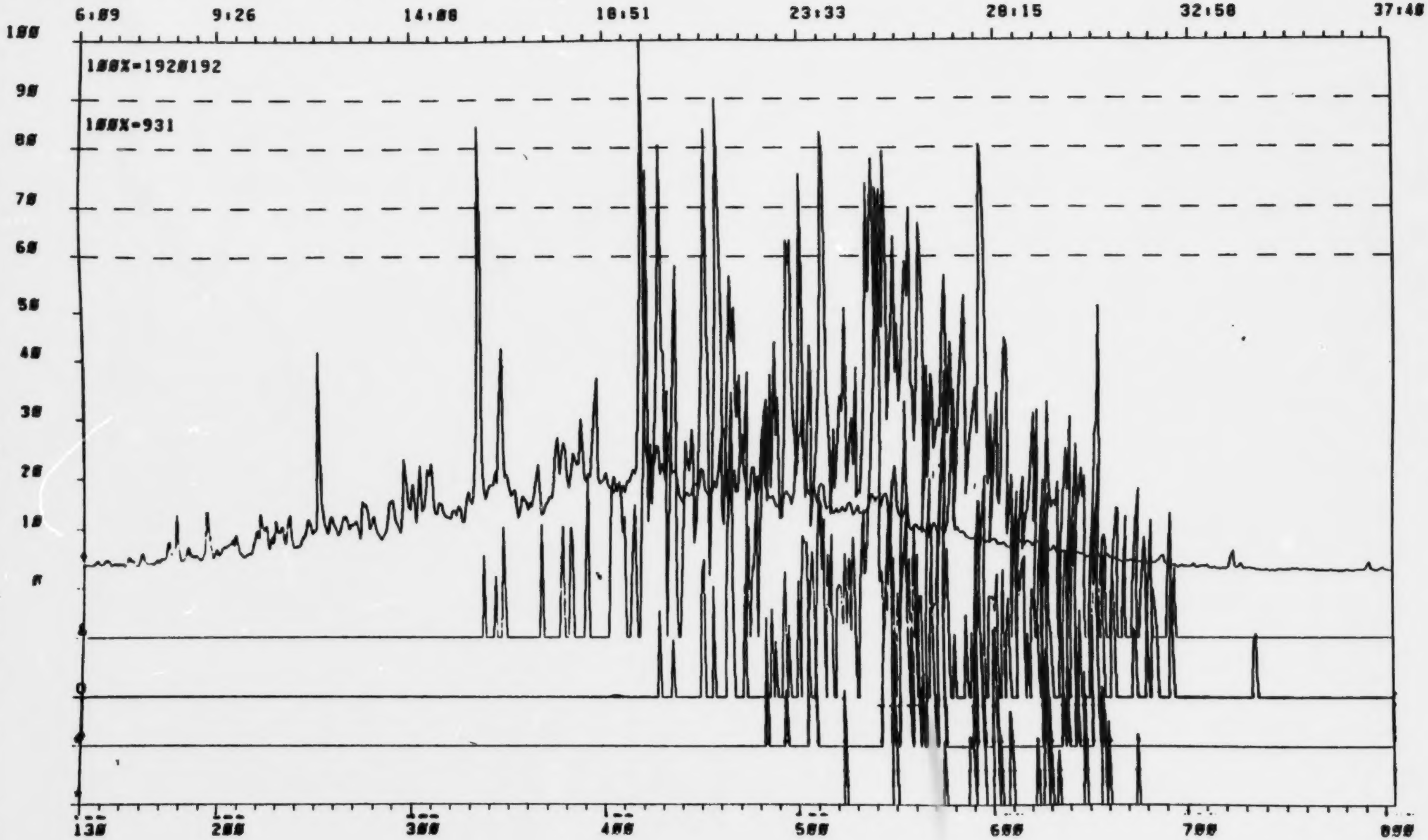


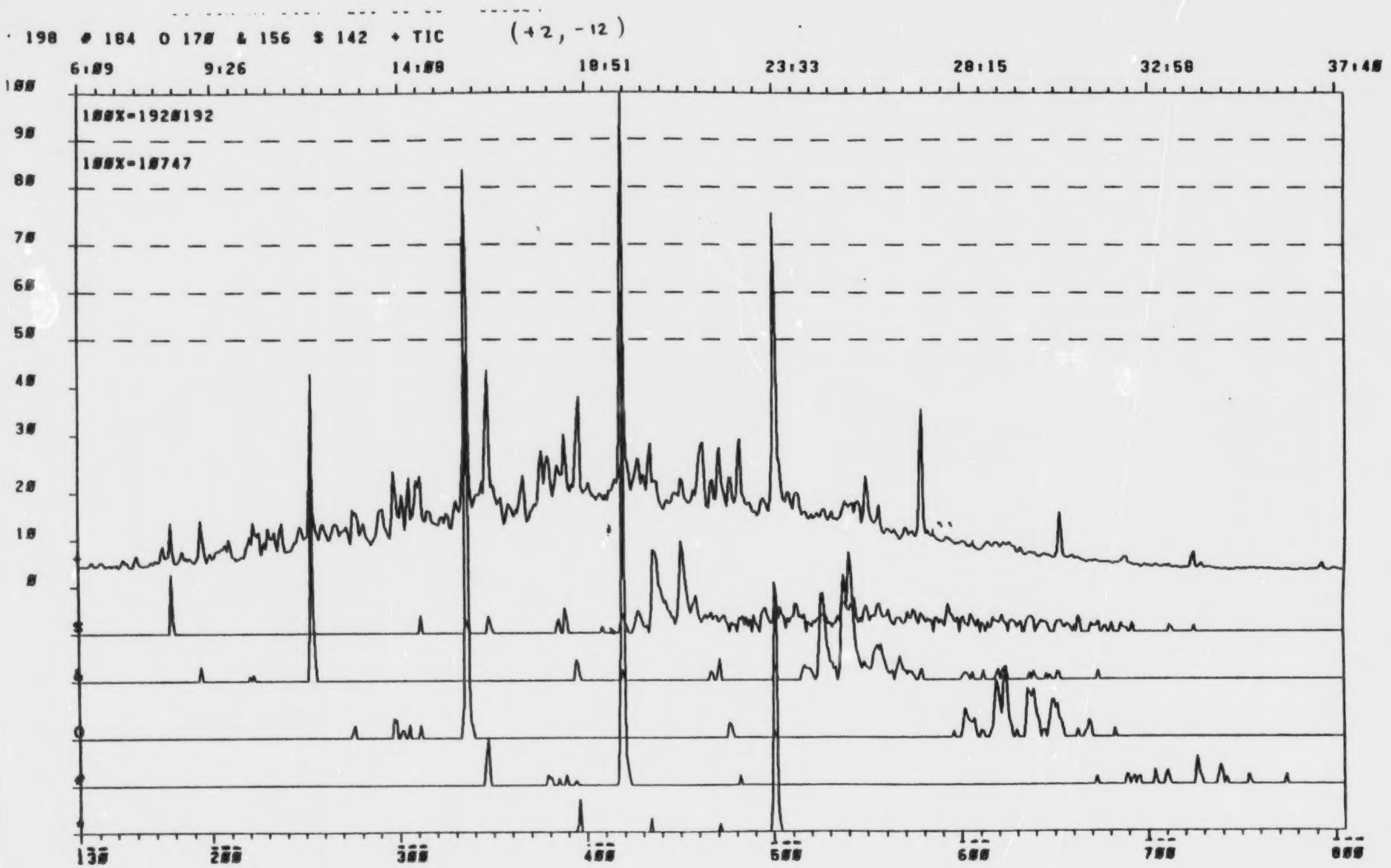
AP2 COMPOSITE SUNCOR HT DIST 261-85-65 860304
* 188 # 174 160 & 146 $ 132 + TIC (-0)



AP2 COMPOSITE SUNCOR HT DIST 261-05-65 060304

* 186 # 172 $ 158 & 144 + TIC (-10)

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600
700
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(Backgnd — bstr.)   1

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                    GULF CANADA RESEARCH AND DEVELOPMENT DEPARTMENT

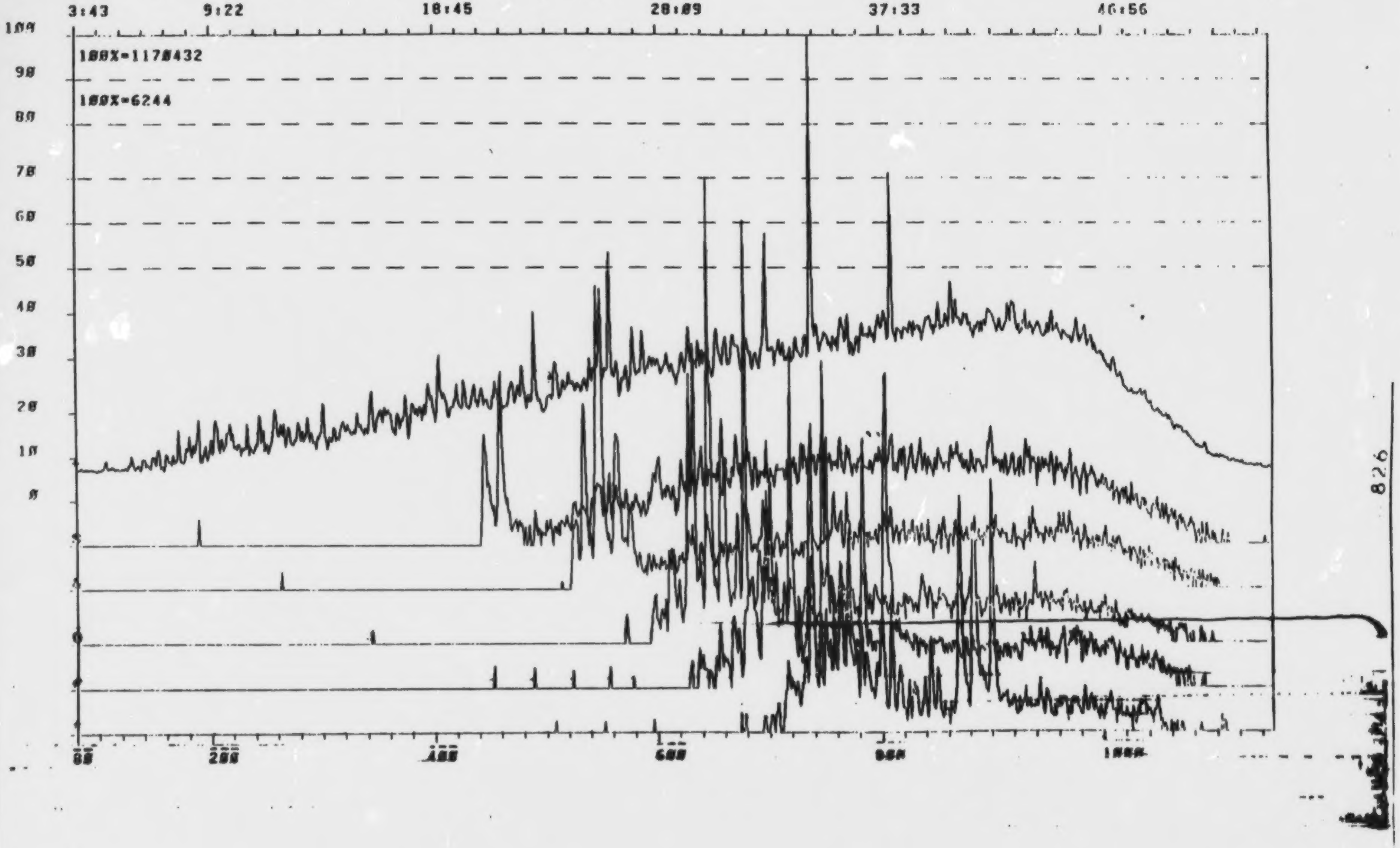
SAMPLE AP3 COMP.      HUSKY FIREFLOODED DIST           ANALYSED: 1986 MAR  11.    11:10
PROJECT NO 261-85                             RUN NUMBER F1055A              METHOD DIST

              DISTILLATE ANALYSIS BY LOW RESOLUTION MASS SPECTROMETRY

                                                  DETERMINED              CALCULATED
   HYDROCARBON TYPE (CN.H2N-Z)        Z NO      VOLUME PERCENT           MASS PERCENT
   SATURATES                                                78.14                   76.15
      PARAFFINS                        +2        14.35                   12.83
     CYCLOPARAFFINS                                   63.79                   63.32
      NONCOND CYCLOPARAFFINS            0        29.33                   27.92
      COND DICYCLOPARAFFINS            -2        24.08                   24.32
      COND POLYCYCLOPARAFFINS          -4        10.37                   11.08
   AROMATICS                                                21.86                   23.85
     MONOAROMATICS                                    15.56                   16.21
      ALKYLBENZENES                    -6         7.21                    7.20
      BENZOCYCLOPARAFFINS              -8         4.09                    4.41
      BENZODICYCLOPARAFFINS           -10         4.26                    4.60
     DIAROMATICS                                       4.20                    4.87
      NAPHTHALENES                    -12         2.98                    3.36
      NAPHTHOCYCLOPARAFFINS           -14         0.37                    0.44
      FLUORENES                       -16         0.86                    1.07
     TRIAROMATICS                                      0.80                    1.10
      PHENANTHRENES/ANTHRACENE        -18         0.68                    0.93
      PHENANTHROCYCLOPARAFFINS        -20         0.12                    0.17
     TETRAAROMATICS                                    0.18                    0.27
      PYRENES/BENZOFLUORENES          -22         0.14                    0.20
      CHRYSENES/BENZANTHRACENE        -24         0.05                    0.07
     PENTAAROMATICS                                    0.00                    0.00
      CHRYSOCYCLOPARAFFINS            -26         0.00                    0.00
      BENZPYRENES/PERYLENES           -28         0.00                    0.00
      DIBENZANTHRACENES               -30         0.00                    0.00
     UNIDENTIFIED                                      0.00                    0.00
      Cn.H2n-32                       -32         0.00                    0.00
      Cn.H2n-36/Cn.H2n-26.S           -36         0.00                    0.00
      Cn.H2n-38/Cn.H2n-28.S           -38         0.00                    0.00
      Cn.H2n-42/Cn.H2n-32.S           -42         0.00                    0.00
      Cn.H2n-44/Cn.H2n-34.S           -44         0.00                    0.00
     AROMATIC SULFUR                                   1.11                    1.41
      BENZOTHIOPHENES                 -10S        1.11                    1.41
      DIBENZOTHIOPHENES               -16S        0.00                    0.00
      BENZONAPHTHOTHIOPHENES          -22S        0.00                    0.00
```

APS COMP. HUSKY FIREFLOODED 160-340C 261-05-65 860305

* 198 # 184 170 & 156 $ 142 + TIC (-12, -165)



826

(Backgnd corrected)

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                    GULF CANADA RESEARCH   DEVELOPMENT DEPARTMENT

SAMPLE AP4 COMP.           WYODAK COAL LIQU.                 ANALYSED: 1986 MAR  11.   14: 3
PROJECT NO 261-85                                   RUN NUMBER F1047A                METHOD DIST

                 DISTILLATE ANALYSIS BY LOW RESOLUTION MASS SPECTROMETRY

                                                    DETERMINED             CALCULATED
   HYDROCARBON TYPE (CN.H2N-Z)       Z NO         VOLUME PERCENT          MASS PERCENT
   SATURATES                                                82.34                  81.12
      PARAFFINS                       +2           2.52                    2.22
    CYCLOPARAFFINS                                      79.83                  78.90
      NONCOND CYCLOPARAFFINS           0          42.03                   39.49
      COND DICYCLOPARAFFINS           -2          30.40                   31.42
      COND POLYCYCLOPARAFFINS         -4           7.40                    7.99
   AROMATICS                                                17.37                  18.88
    MONOAROMATICS                                       15.77                  16.97
      ALKYLBENZENES                   -6           5.94                    6.00
      BENZOCYCLOPARAFFINS             -8           9.14                   10.20
      BENZODICYCLOPARAFFINS          -10           0.69                    0.77
    DIAROMATICS                                          1.60                   1.91
      NAPHTHALENES                   -12           1.30                    1.52
      NAPHTHOCYCLOPARAFFINS          -14           0.30                    0.38
      FLUORENES                      -16           0.00                    0.00
    TRIAROMATICS                                         0.00                   0.00
      PHENANTHRENES/ANTHRACENE       -18           0.00                    0.00
      PHENANTHROCYCLOPARAFFINS       -20           0.00                    0.00
    TETRAAROMATICS                                       0.00                   0.00
      PYRENES/BENZOFLUORENES         -22           0.00                    0.00
      CHRYSENES/BENZANTHRACENE       -24           0.00                    0.00
    PENTAAROMATICS                                       0.00                   0.00
      CHRYSOCYCLOPARAFFINS           -26           0.00                    0.00
      BENZPYRENES/PERYLENES          -28           0.00                    0.00
      DIBENZANTHRACENES              -30           0.00                    0.00
    UNIDENTIFIED                                         0.00                   0.00
      Cn.H2n-32                      -32           0.00                    0.00
      Cn.H2n-36/Cn.H2n-26.S          -36           0.00                    0.00
      Cn.H2n-38/Cn.H2n-28.S          -38           0.00                    0.00
      Cn.H2n-42/Cn.H2n-32.S          -42           0.00                    0.00
      Cn.H2n-44/Cn.H2n-34.S          -44           0.00                    0.00
    AROMATIC SULFUR                                      0.00                   0.00
      BENZOTHIOPHENES                -10S          0.00                    0.00
      DIBENZOTHIOPHENES              -16S          0.00                    0.00
      BENZONAPHTHOTHIOPHENES         -22S          0.00                    0.00
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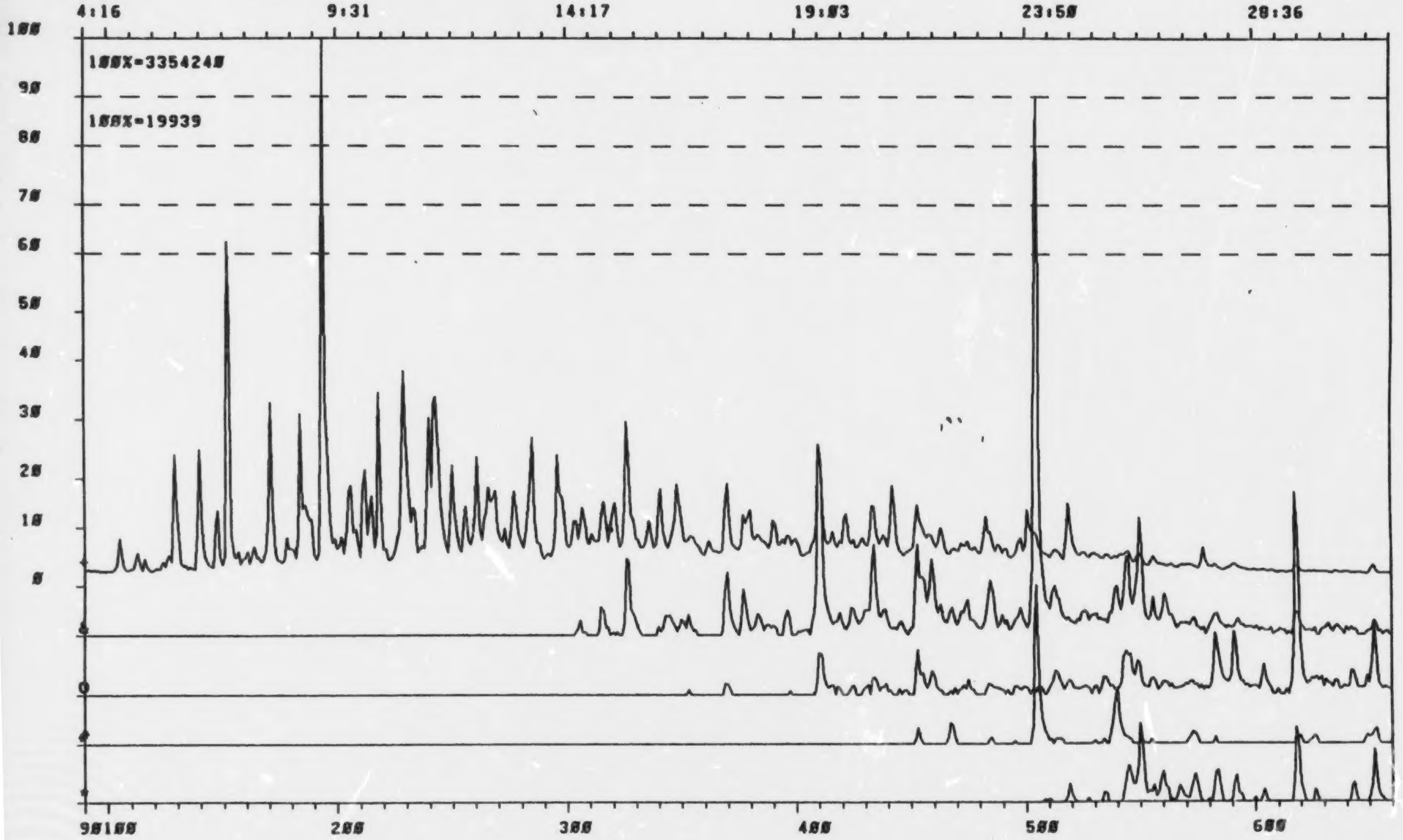
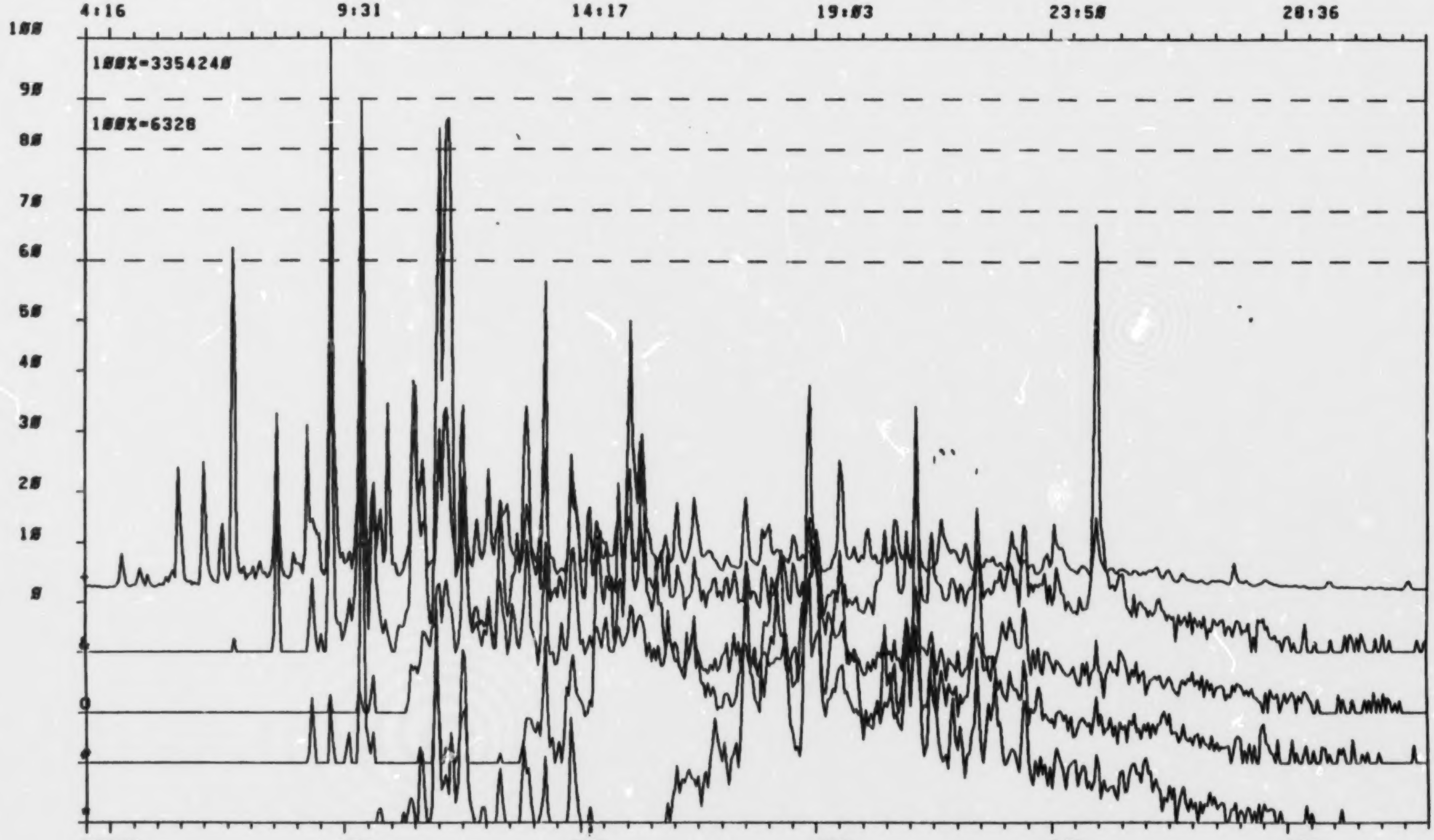
AP4 COMPOSITE WYODAK LIQU. COAL (176-257C) 261-85-65 860304

* 172 # 158 O 144 & 130 + TIC



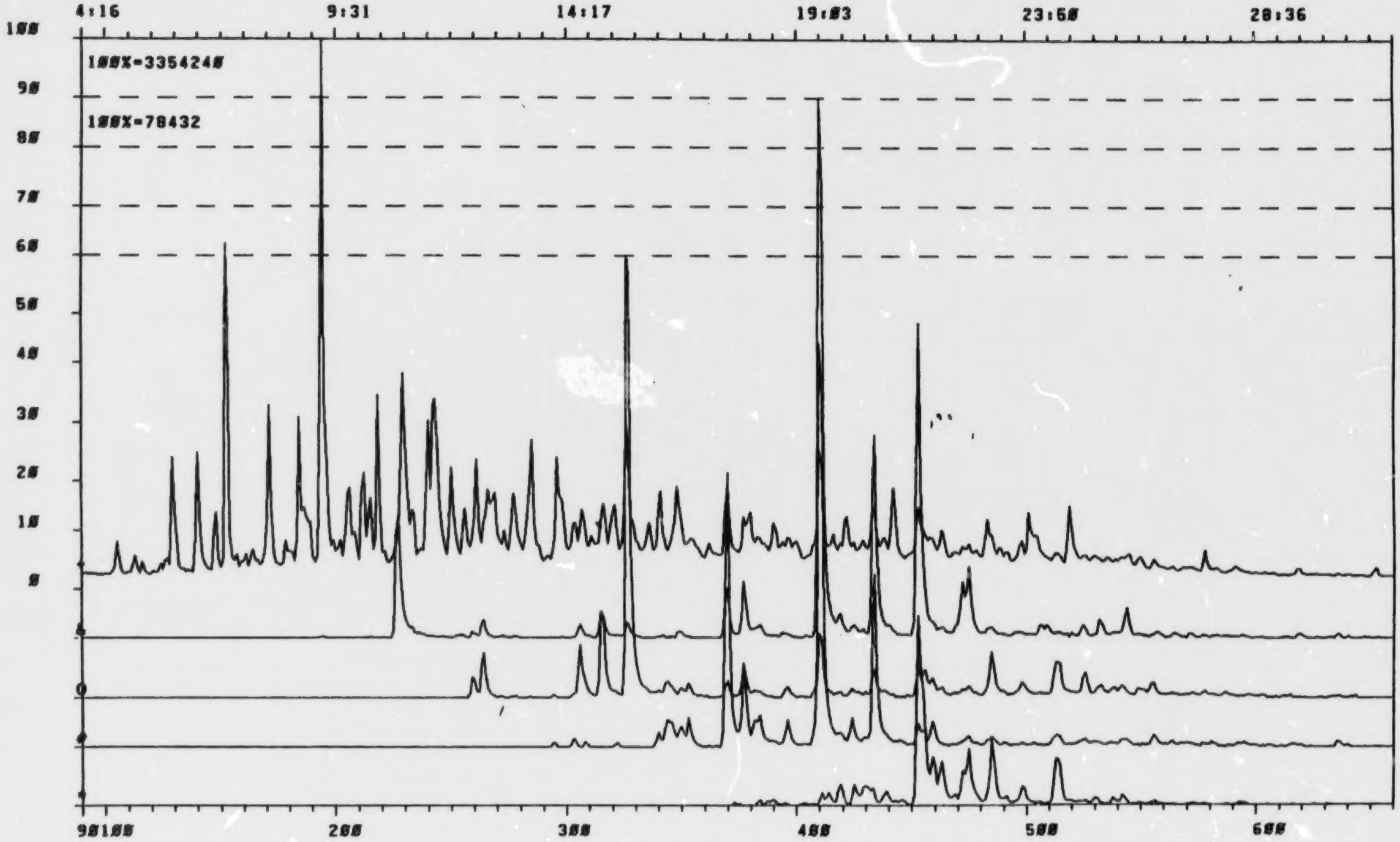
DS-55 CROSS SCAN REPORT, RUN: 3F1047
AP4 COMPOS 2 WYODAK LIQU. COAL (176-257C) 261-85-65 860304
* 136 # 122 O 108 & 94 + TIC (-60 phenols)



85-85 CROSS [illegible]AN REPORT, RUN: SF1047

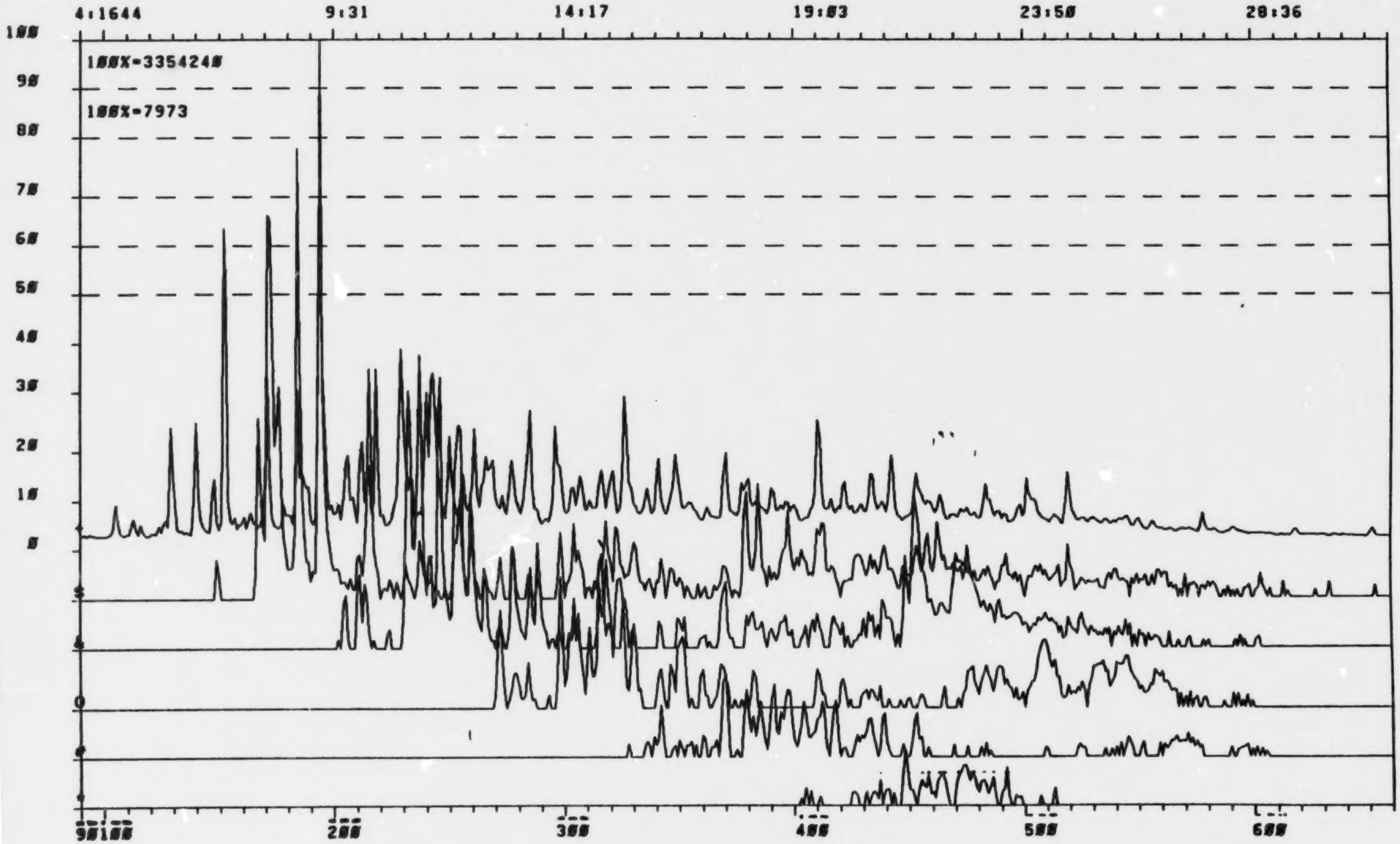
AP4 COMPOSITE WYODAK LIQU. COAL (176-257C) 261-85-65 860304

* 160 # 146 O 132 & 118 + TIC (-8)



AP4 COMPOSITE WYODAK LIQU. COAL (176-257C) 261-85-65 860304

* 176 # 162 O 148 & 134 $ 120 + TIC (-6)



(Bad orrected)

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                    GULF CANADA RESEARCH   D DEVELOPMENT DEPARTMENT

SAMPLE AP5 COMP.                COMMERCIAL DIESEL              ANALYSED: 1986 MAR  11.    13:57
PROJECT NO 261-85                                       RUN NUMBER F1051A               METHOD DIST

                    DISTILLATE ANALYSIS BY LOW RESOLUTION MASS SPECTROMETRY

                                                       DETERMINED                CALCULATED
    HYDROCARBON TYPE (CN.H2N-Z)         Z NO         VOLUME PERCENT            MASS PERCENT
    SATURATES                                                   84.69                     83.05
        PARAFFINS                        +2          44.48                     41.84
      CYCLOPARAFFINS                                       40.20                     41.22
        NONCOND CYCLOPARAFFINS            0          28.31                     28.38
        COND DICYCLOPARAFFINS            -2          11.22                     12.07
        COND POLYCYCLOPARAFFINS          -4           0.67                      0.76
    AROMATICS                                                   15.30                     16.95
      MONOAROMATICS                                        12.99                     14.08
        ALKYLBENZENES                    -6          10.36                     11.03
        BENZOCYCLOPARAFFINS              -8           2.28                      2.65
        BENZODICYCLOPARAFFINS           -10           0.35                      0.41
      DIAROMATICS                                           2.31                      2.86
        NAPHTHALENES                    -12           2.31                      2.86
        NAPHTHOCYCLOPARAFFINS           -14           0.00                      0.00
        FLUORENES                       -16           0.00                      0.00
      TRIAROMATICS                                          0.00                      0.00
        PHENANTHRENES/ANTHRACENE        -18           0.00                      0.00
        PHENANTHROCYCLOPARAFFINS        -20           0.00                      0.00
      TETRAAROMATICS                                        0.00                      0.00
        PYRENES/BENZOFLUORENES          -22           0.00                      0.00
        CHRYSENES/BENZANTHRACENE        -24           0.00                      0.00
      PENTAAROMATICS                                        0.00                      0.00
        CHRYSOCYCLOPARAFFINS            -26           0.00                      0.00
        BENZPYRENES/PERYLENES           -28           0.00                      0.00
        DIBENZANTHRACENES               -30           0.00                      0.00
      UNIDENTIFIED                                          0.00                      0.00
        Cn.H2n-32                       -32           0.00                      0.00
        Cn.H2n-36/Cn.H2n-26.S           -36           0.00                      0.00
        Cn.H2n-38/Cn.H2n-28.S           -38           0.00                      0.00
        Cn.H2n-42/Cn.H2n-32.S           -42           0.00                      0.00
        Cn.H2n-44/Cn.H2n-34.S           -44           0.00                      0.00
      AROMATIC SULFUR                                       0.00                      0.00
        BENZOTHIOPHENES                 -10S          0.00                      0.00
        DIBENZOTHIOPHENES               -16S          0.00                      0.00
        BENZONAPHTHOTHIOPHENES          -22S          0.00                      0.00
```
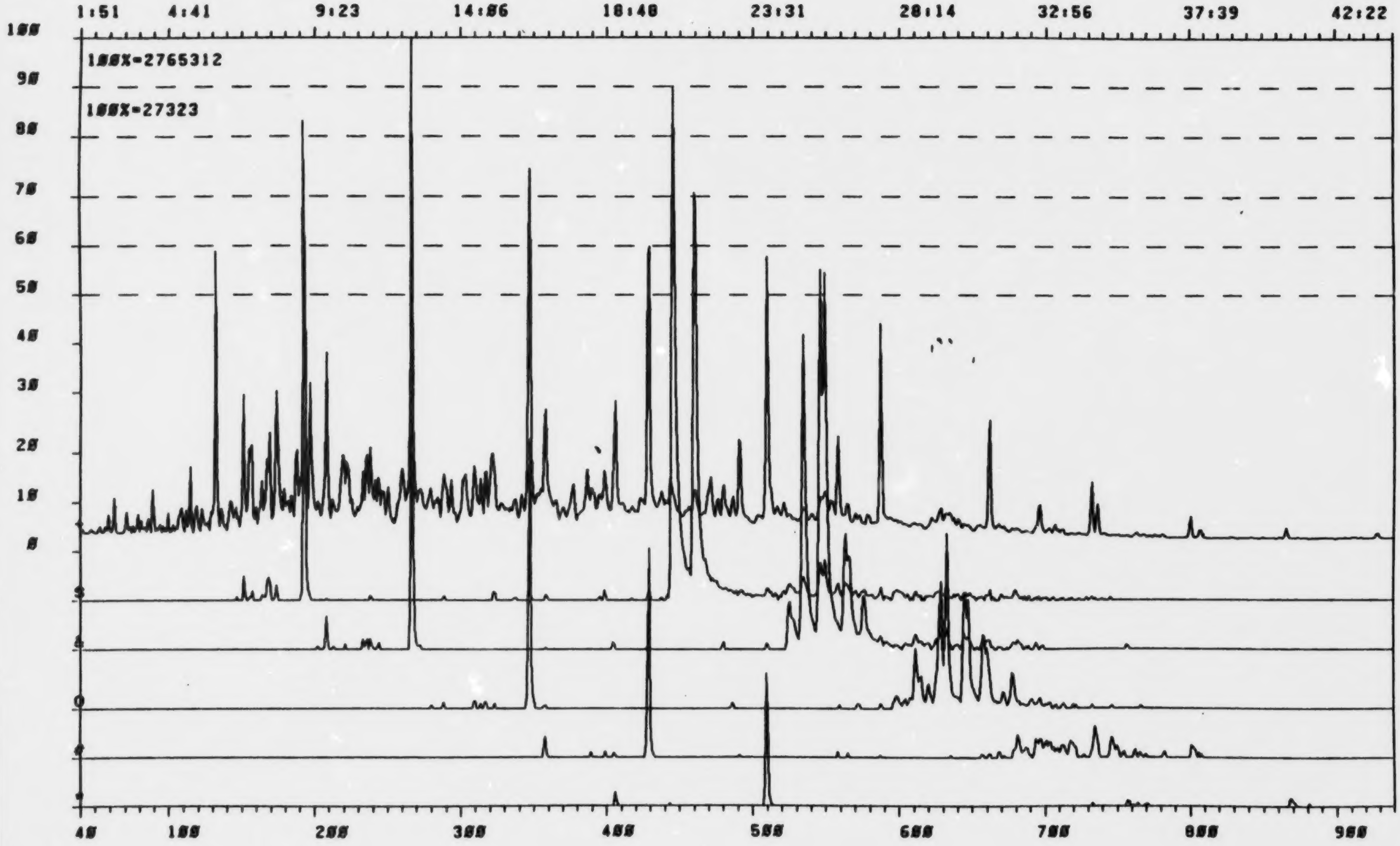

DS-55 CROSS SCAN REPORT, RUN: 3F1051

AP5 COMPOSITE COMM. DIESEL 261-85-65 860304

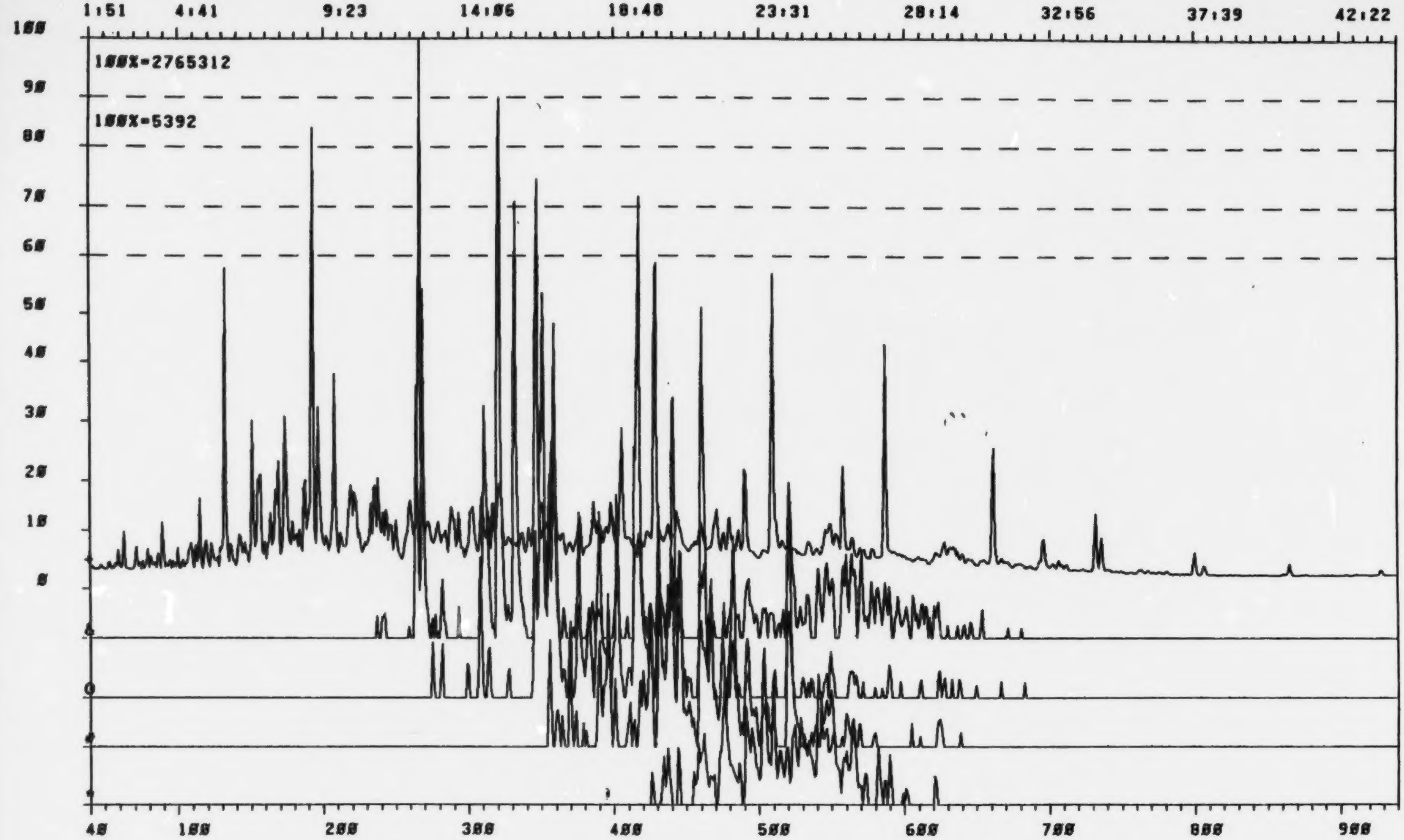
* 198 # 184 O 170 & 156 $ 142 + TIC (+2., -12)



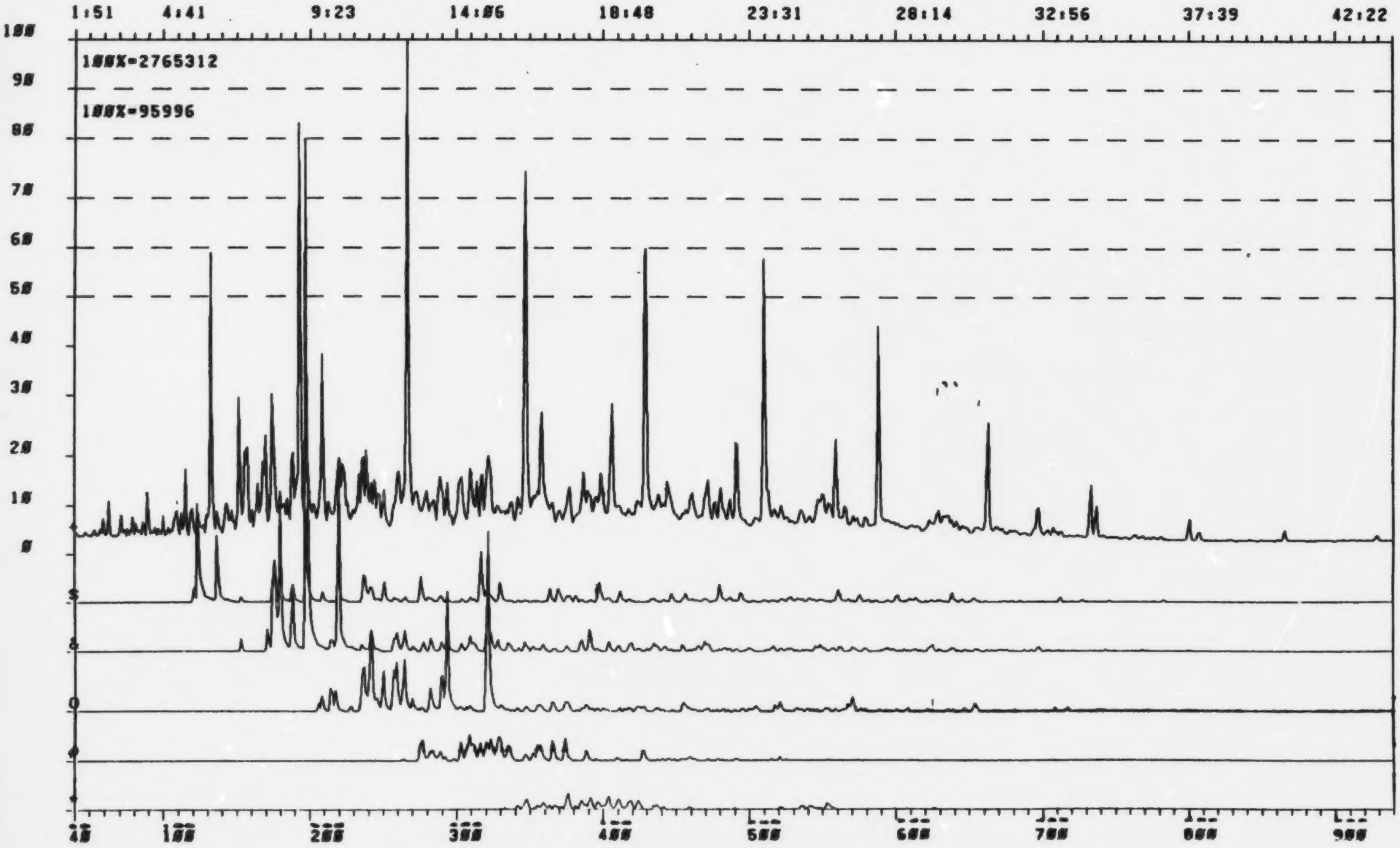
05-05 CROSS AN REPORT, RUN: 3F1051

AP5 COMPOSITE COMM. DIESEL 261-85-65 860304

* 174 # 160 O 146 & 132 + TIC (-8)

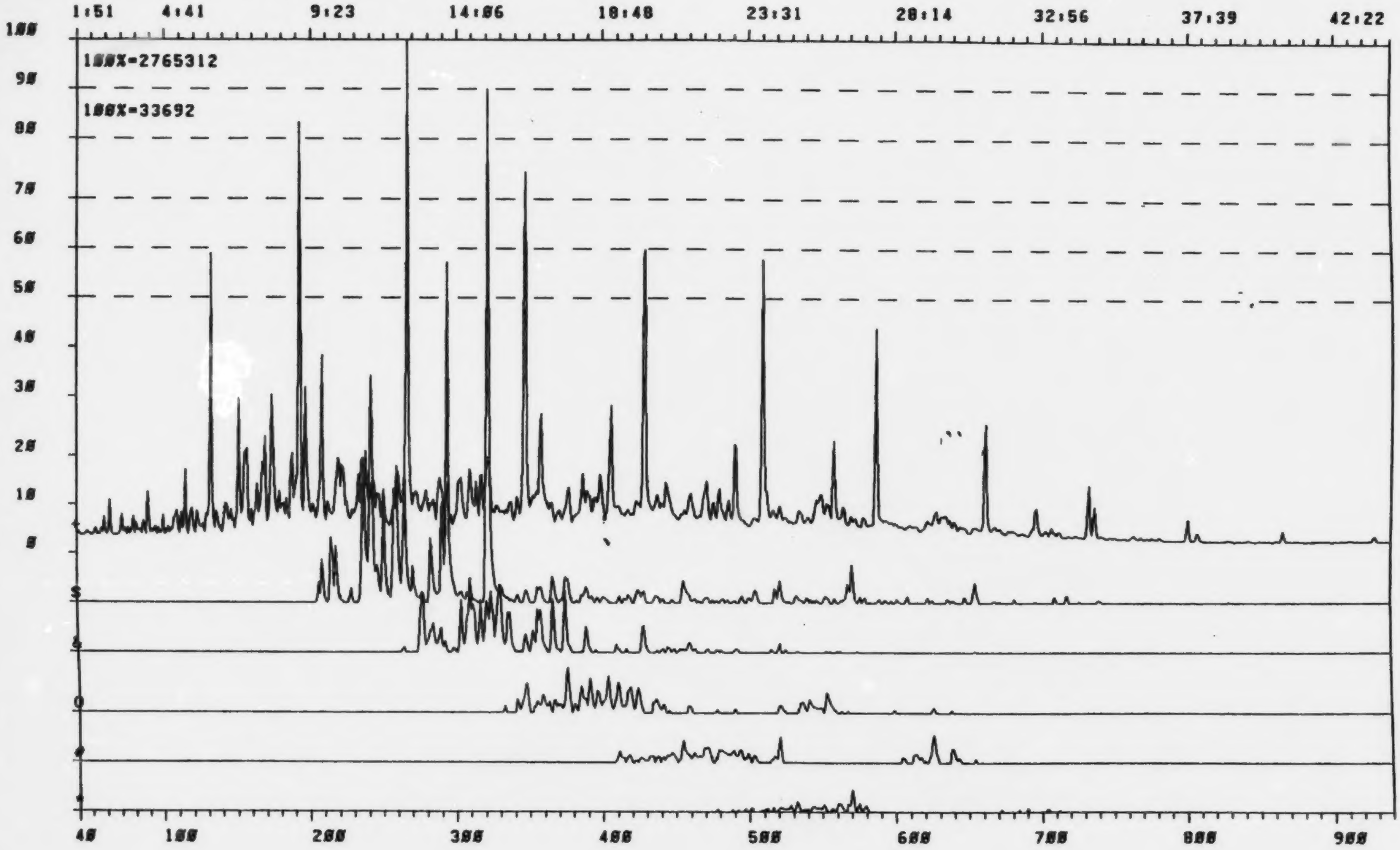


DS-55 CROSS SCAN REPORT. RUN: 3F1051
AP5 COMPOSITE COMM. DIESEL 261-85-65 860304
* 162 # 148 O 134 & 120 $ 106 + TIC (-6, -105)



AP5 COMPOSI.. COMM. DIESEL 261-85-65 860304

* 190 # 176 O 162 & 148 $ 134 + TIC (-6, -105)



(Backgnd [illegible]cted)

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                    GULF CANADA RESEARCH AND DEVELOPMENT DEPARTMENT

SAMPLE AP6 COMP.          SYNCRUDE EFV O/H                  ANALYSED: 1986 MAR  11.    13:51
PROJECT NO 261-85                                  RUN NUMBER F1056A              METHOD DIST

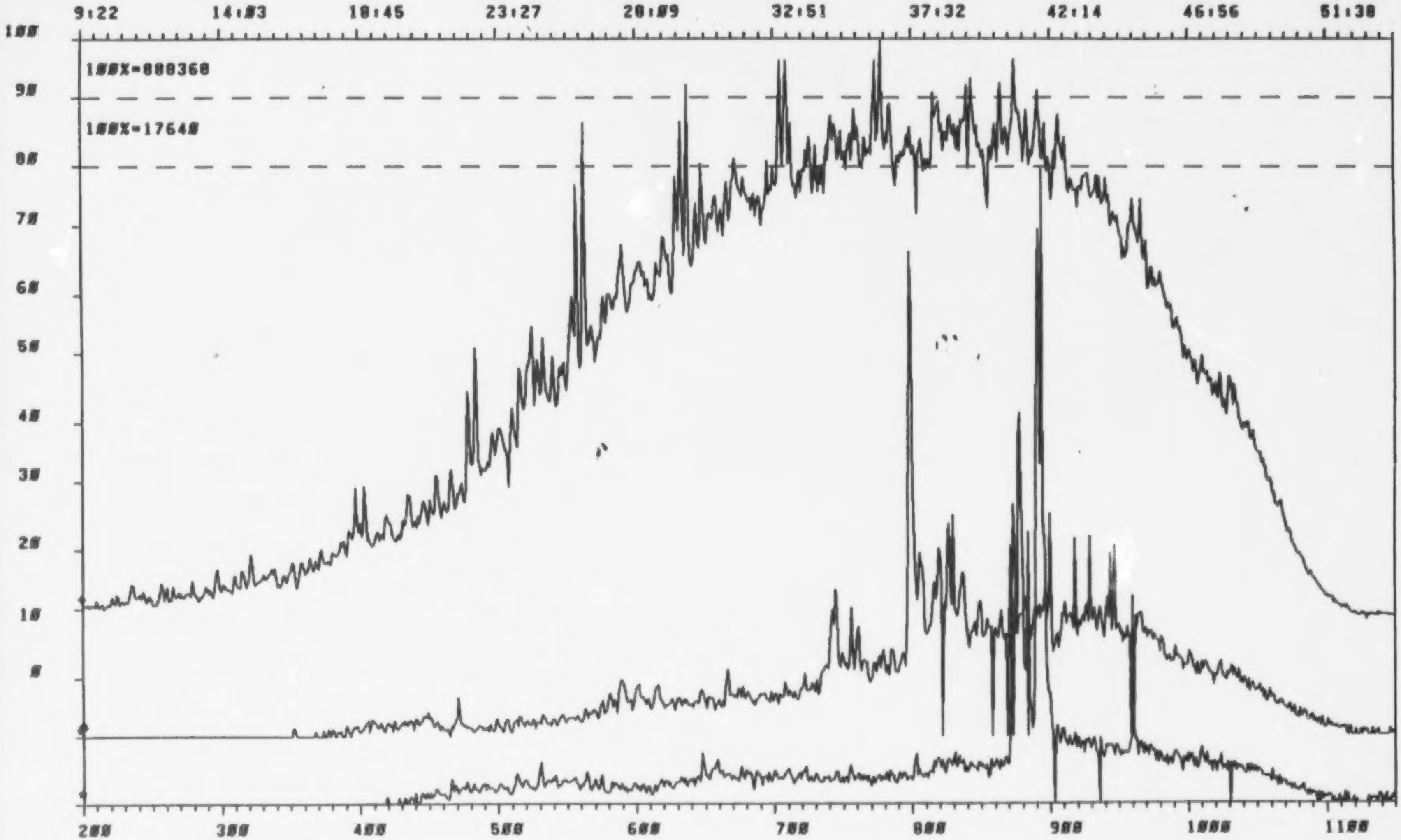
                 DISTILLATE ANALYSIS BY LOW RESOLUTION MASS SPECTROMETRY

                                                  DETERMINED                CALCULATED
    HYDROCARBON TYPE (CN.H2N-Z)      Z NO        VOLUME PERCENT            MASS PERCENT
    SATURATES                                              65.10                    62.79
      PARAFFINS                       +2         4.23                     3.72
      CYCLOPARAFFINS                                  60.87                    59.07
        NONCOND CYCLOPARAFFINS         0        25.92                    23.97
        COND DICYCLOPARAFFINS         -2        20.70                    20.31
        COND POLYCYCLOPARAFFINS       -4        14.25                    14.78
    AROMATICS                                              34.90                    37.21
      MONOAROMATICS                                   21.17                    21.42
        ALKYLBENZENES                 -6         8.05                     7.81
        BENZOCYCLOPARAFFINS           -8         5.93                     6.16
        BENZODICYCLOPARAFFINS        -10         7.18                     7.45
      DIAROMATICS                                      8.39                     9.30
        NAPHTHALENES                 -12         4.56                     4.89
        NAPHTHOCYCLOPARAFFINS        -14         1.82                     2.05
        FLUORENES                    -16         2.01                     2.36
      TRIAROMATICS                                     1.05                     1.30
        PHENANTHRENES/ANTHRACENE     -18         1.05                     1.29
        PHENANTHROCYCLOPARAFFINS     -20         0.00                     0.01
      TETRAAROMATICS                                   0.38                     0.54
        PYRENES/BENZOFLUORENES       -22         0.36                     0.50
        CHRYSENES/BENZANTHRACENE     -24         0.02                     0.04
      PENTAAROMATICS                                   0.00                     0.00
        CHRYSOCYCLOPARAFFINS         -26         0.00                     0.00
        BENZPYRENES/PERYLENES        -28         0.00                     0.00
        DIBENZANTHRACENES            -30         0.00                     0.00
      UNIDENTIFIED                                     0.00                     0.00
        Cn.H2n-32                    -32         0.00                     0.00
        Cn.H2n-36/Cn.H2n-26.S        -36         0.00                     0.00
        Cn.H2n-38/Cn.H2n-28.S        -38         0.00                     0.00
        Cn.H2n-42/Cn.H2n-32.S        -42         0.00                     0.00
        Cn.H2n-44/Cn.H2n-34.S        -44         0.00                     0.00
      AROMATIC SULFUR                                  3.90                     4.66
        BENZOTHIOPHENES              -10S        3.68                     4.36
        DIBENZOTHIOPHENES            -16S        0.18                     0.25
        BENZONAPHTHOTHIOPHENES       -22S        0.04                     0.05
```

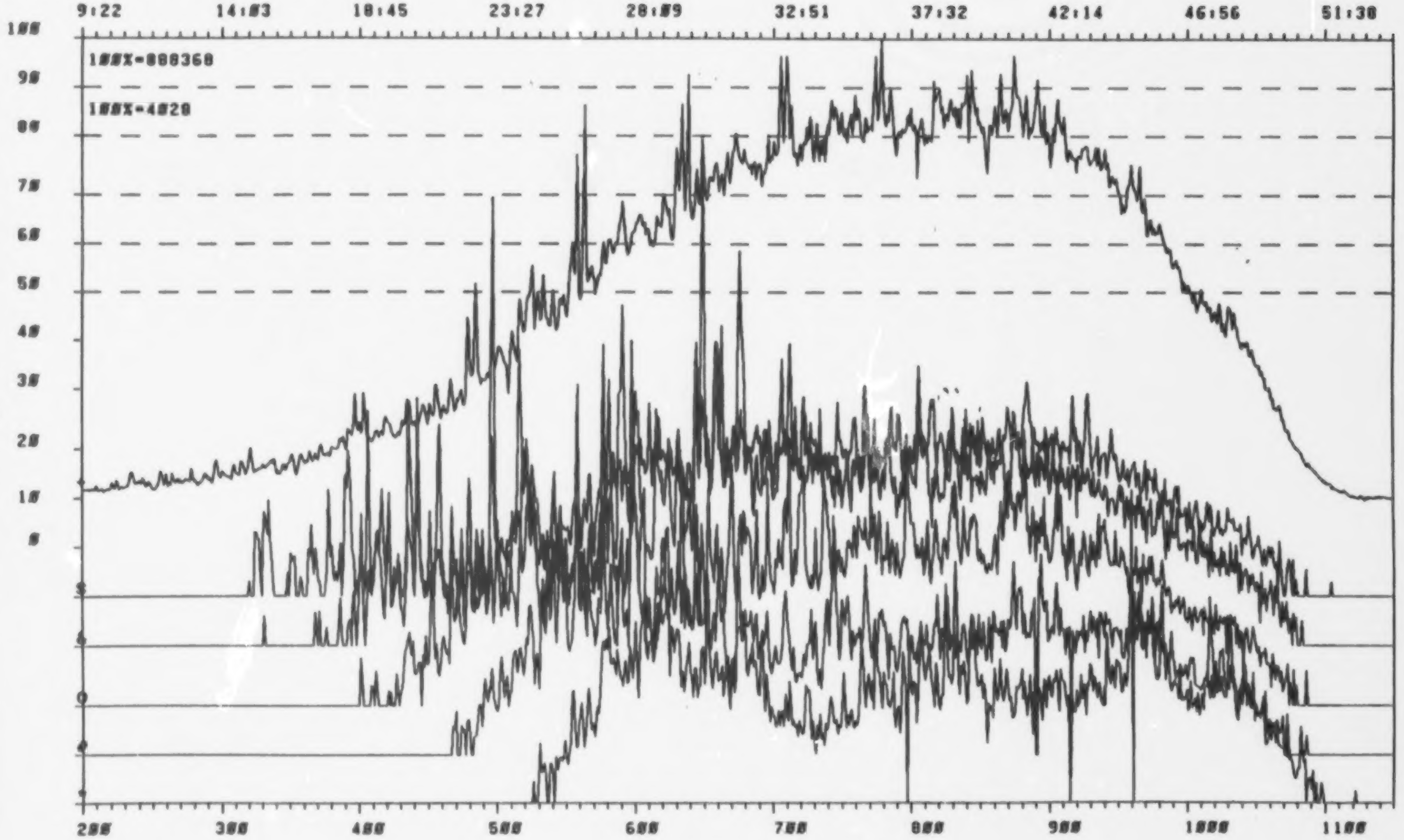
DS-55 CROSS SCAN REPORT, RUN: 3F1056

AP6 COMPOSITE SYNCRUDE EFV O/H 252-346C 261-85-65 860305

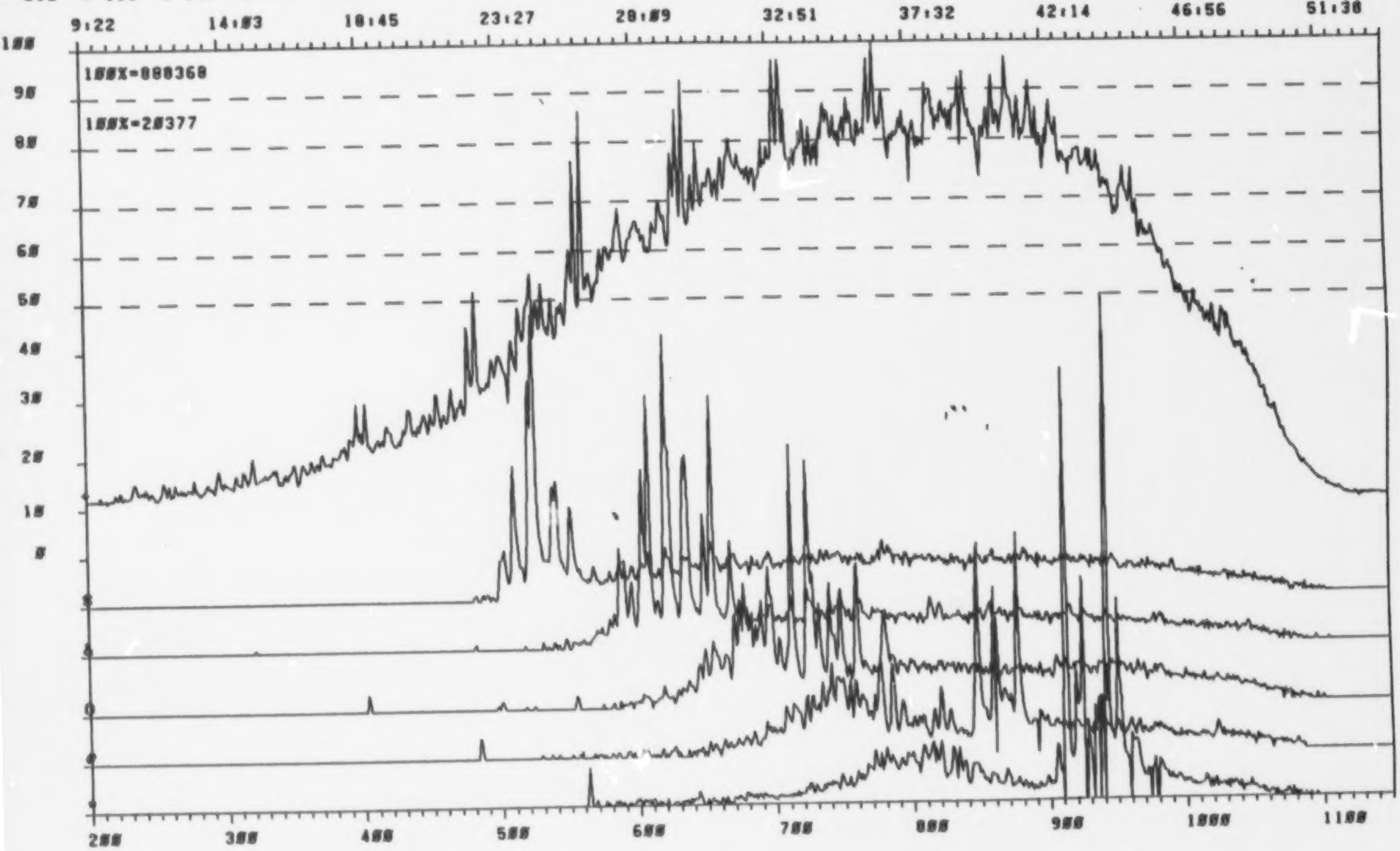
* 192 # 178 + TIC



DS-55 CROSS SCAN REPORT. RUN: 3F1056
AP6 COMPOSITE SYNCRUDE EFV O/H 252-346C 261-85-65 860305
* 202 # 188 O 174 & 160 $ 146 + TIC



DS-55 CROSS SCAN REPORT, RUN: 3F1056
APG COMPOSITE SYNCRUDE EFV O/H 252-346C 261-05-65 060306
* 212 # 198 O 184 & 170 $ 156 + TIC (+2, -12, -105)

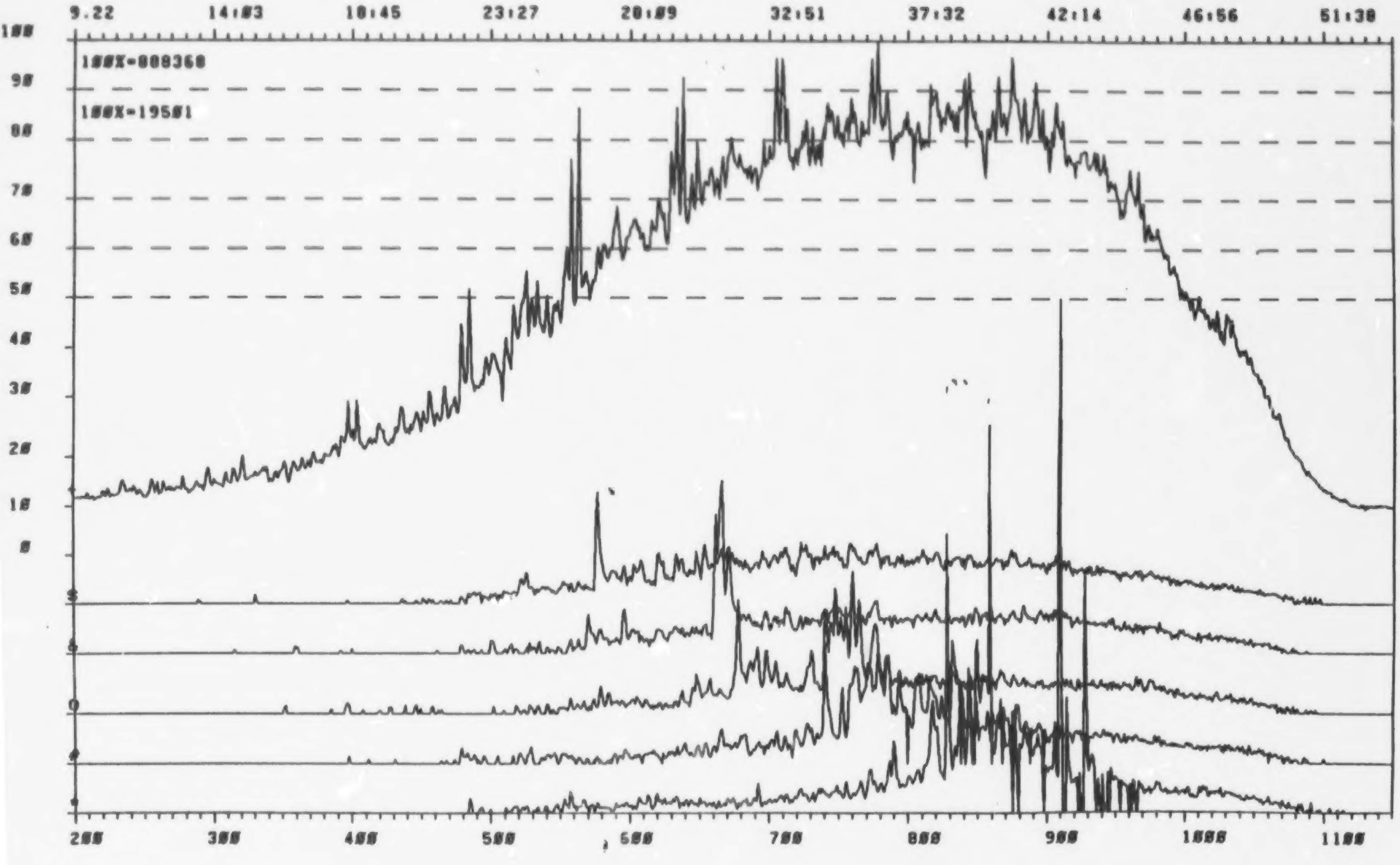


DS-55 CROSS SCAN REPORT, RUN: 3F1056

AP6 COMPOSITE SYNCRUDE EFV O/H 252-346C 261-05-65 060305

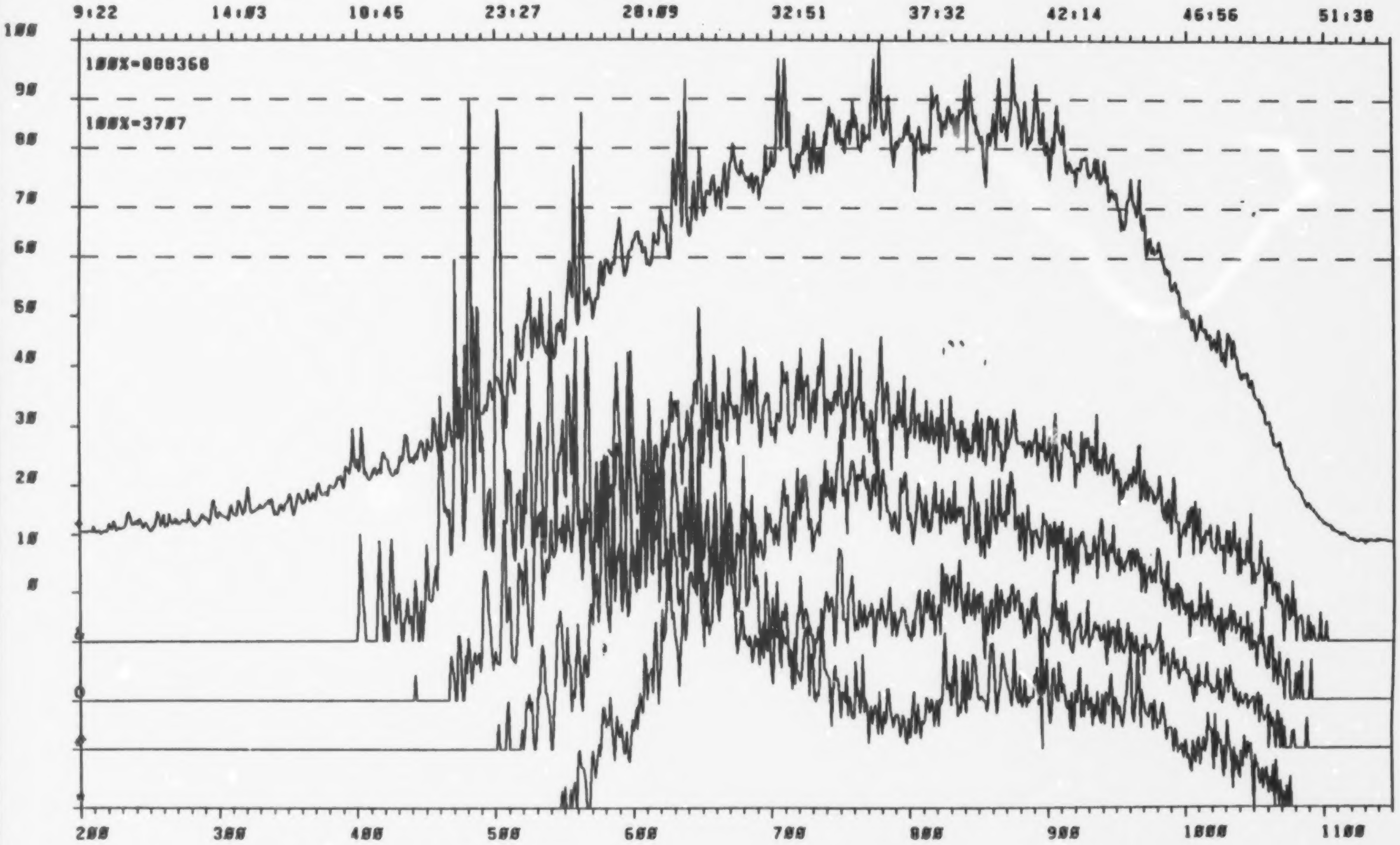
* 210 # 196 O 182 & 168 $ 154 + TIC

(0, -14, -160)



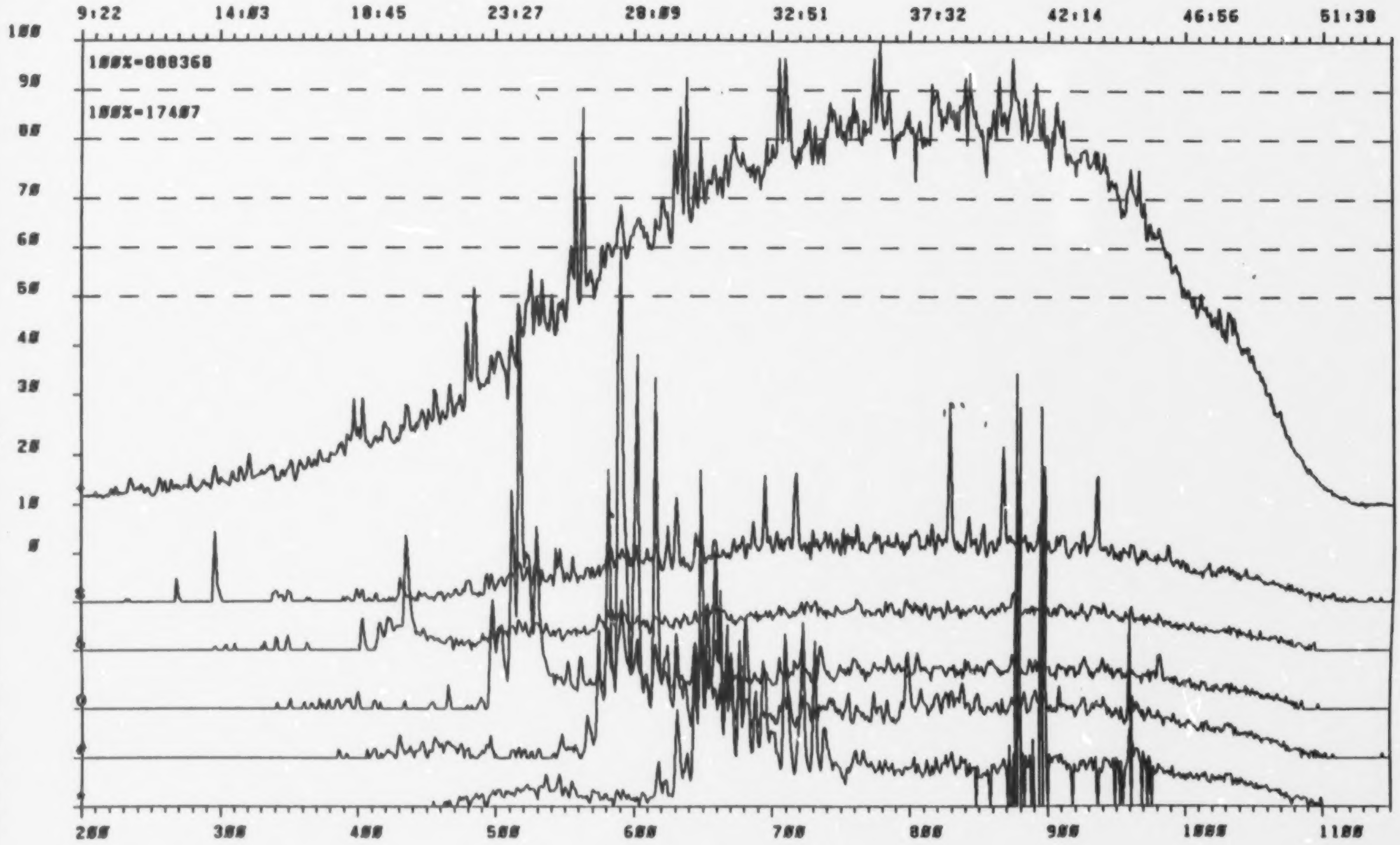
AP6 COMPOSITE SYNCRUDE EFV O/H 252-346C 261-85-65 860305

* 200 # 106 O 172 & 158 + TIC (−10)



AP6 COMPOSITE SYNCRUDE EFV O/H 252-346C 261-85-65 860305

* 190 # 176 O 162 & 148 $ 134 + TIC (-6, -105)



(backgnd. corrected)

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                         GULF CANADA RESEARCH & DEVELOPMENT DEPARTMENT

SAMPLE AP7 COMP.              EDMONTON COKER DIST.          ANALYSED: 1986 MAR  11.    8:56
PROJECT NO 261-85-65                                RUN NUMBER F1050A             METHOD DIST

                    DISTILLATE ANALYSIS BY LOW RESOLUTION MASS SPECTROMETRY

                                                    DETERMINED            CALCULATED
   HYDROCARBON TYPE (CN.H2N-Z)        Z NO        VOLUME PERCENT         MASS PERCENT
   SATURATES                                                 81.59                 79.30
       PARAFFINS                       +2          42.47                39.24
     CYCLOPARAFFINS                                     39.12                 40.05
       NONCOND CYCLOPARAFFINS           0          25.34                24.97
       COND DICYCLOPARAFFINS           -2          11.05                11.99
       COND POLYCYCLOPARAFFINS         -4           2.73                 3.09
   AROMATICS                                                 18.41                 20.70
     MONOAROMATICS                                      15.33                 16.90
       ALKYLBENZENES                   -6           9.41                 9.97
       BENZOCYCLOPARAFFINS             -8           4.80                 5.62
       BENZODICYCLOPARAFFINS          -10           1.12                 1.31
     DIAROMATICS                                         3.09                  3.81
       NAPHTHALENES                   -12           3.09                 3.81
       NAPHTHOCYCLOPARAFFINS          -14           0.00                 0.00
       FLUORENES                      -16           0.00                 0.00
     TRIAROMATICS                                        0.00                  0.00
       PHENANTHRENES/ANTHRACENE       -18           0.00                 0.00
       PHENANTHROCYCLOPARAFFINS       -20           0.00                 0.00
     TETRAAROMATICS                                      0.00                  0.00
       PYRENES/BENZOFLUORENES         -22           0.00                 0.00
       CHRYSENES/BENZANTHRACENE       -24           0.00                 0.00
     PENTAAROMATICS                                      0.00                  0.00
       CHRYSOCYCLOPARAFFINS           -26           0.00                 0.00
       BENZPYRENES/PERYLENES          -28           0.00                 0.00
       DIBENZANTHRACENES              -30           0.00                 0.00
     UNIDENTIFIED                                        0.00                  0.00
       Cn.H2n-32                      -32           0.00                 0.00
       Cn.H2n-36/Cn.H2n-26.S          -36           0.00                 0.00
       Cn.H2n-38/Cn.H2n-28.S          -38           0.00                 0.00
       Cn.H2n-42/Cn.H2n-32.S          -42           0.00                 0.00
       Cn.H2n-44/Cn.H2n-34.S          -44           0.00                 0.00
     AROMATIC SULFUR                                     0.00                  0.00
       BENZOTHIOPHENES               -10S           0.00                 0.00
       DIBENZOTHIOPHENES             -16S           0.00                 0.00
       BENZONAPHTHOTHIOPHENES        -22S           0.00                 0.00
```
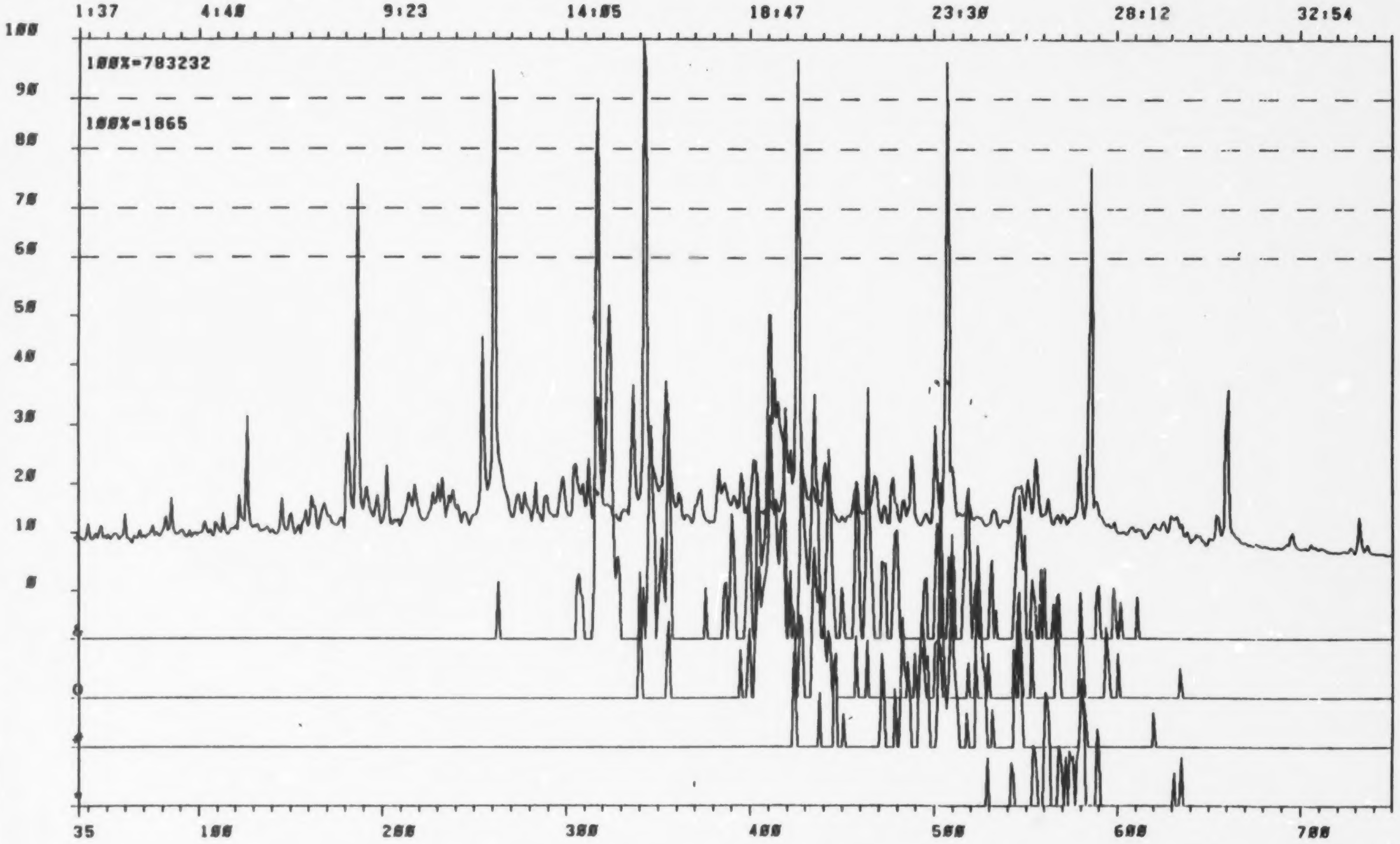

MS CROSS SCAN REPORT, RUN 3F1050

COMPOSITE EDM. COKER DIST 162-277C 261-85-65 860304

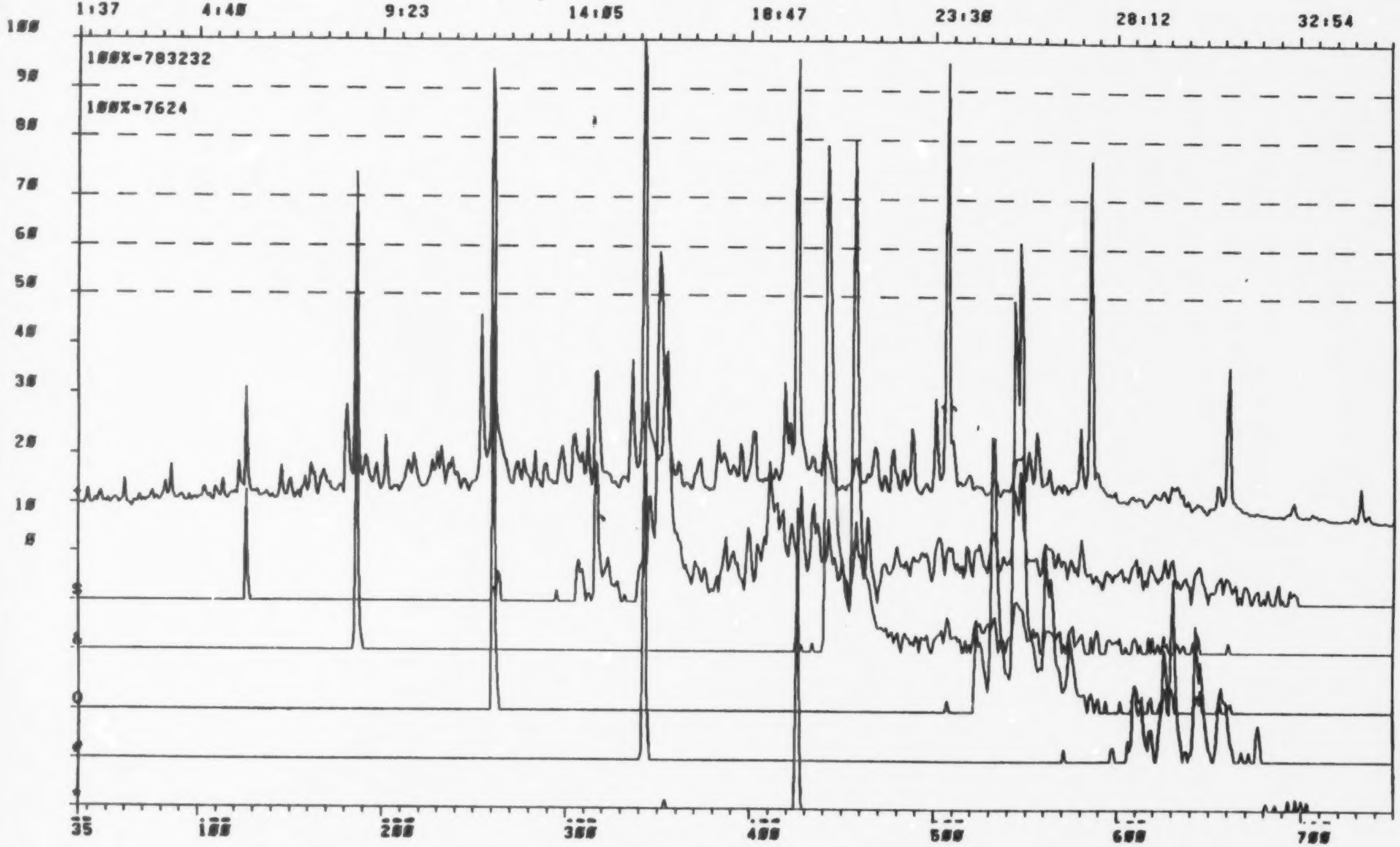
* 172 # 158 O 144 & 130 + TIC (−10)



CROSS SCAN REPORT, RUN# SP1050

.. 7 COMPOSITE EDM. COKER DIST 162-277C 261-05-65 860304

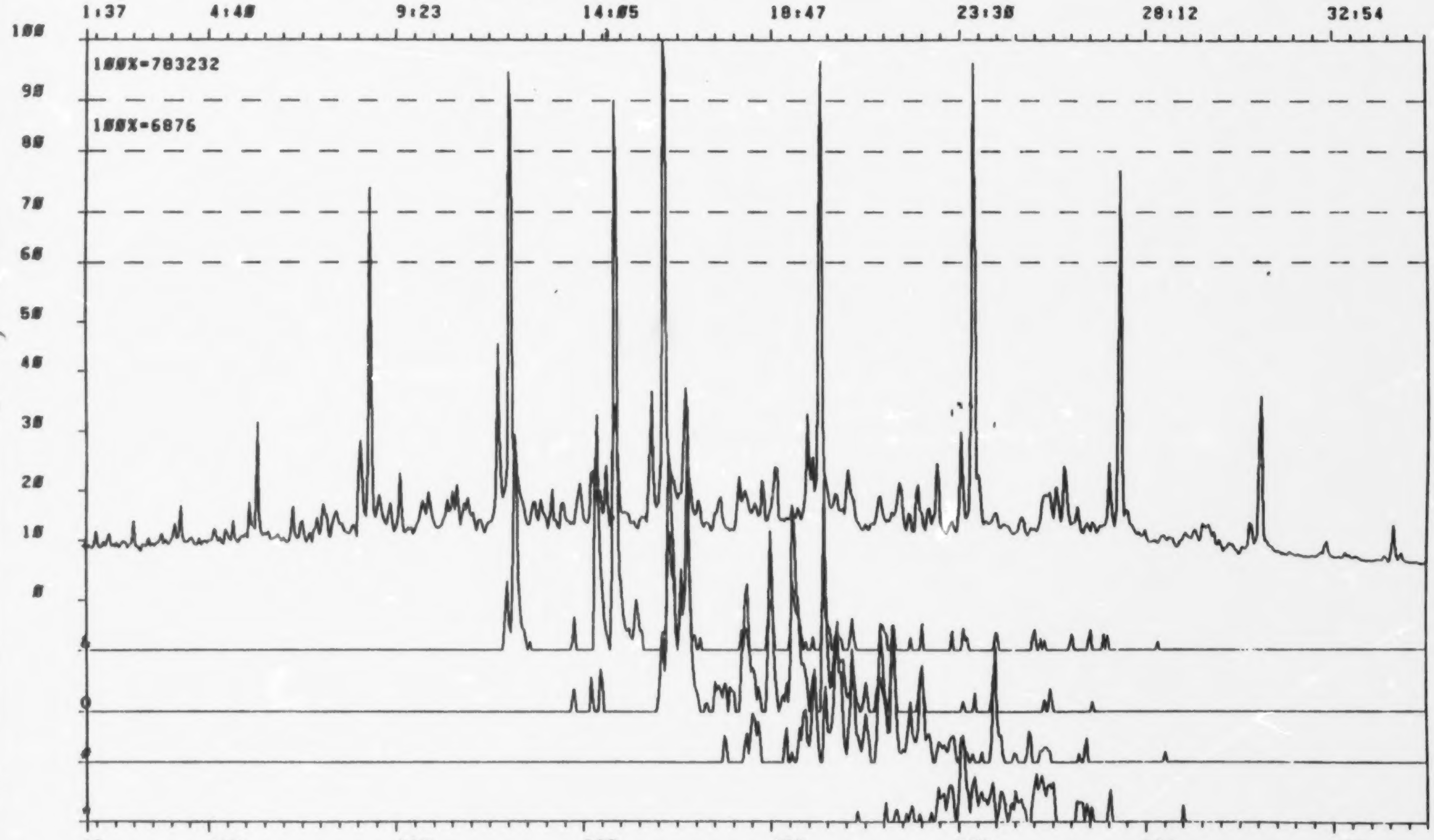
* 104 ø 170 O 156 & 142 $ 128 + TIC (+2∫-12)



-55 CROSS SCAN REPORT, RUN: 3F1050

..P7 COMPOSITE EDM. COKER DIST 162-277C 261-85-65 860304

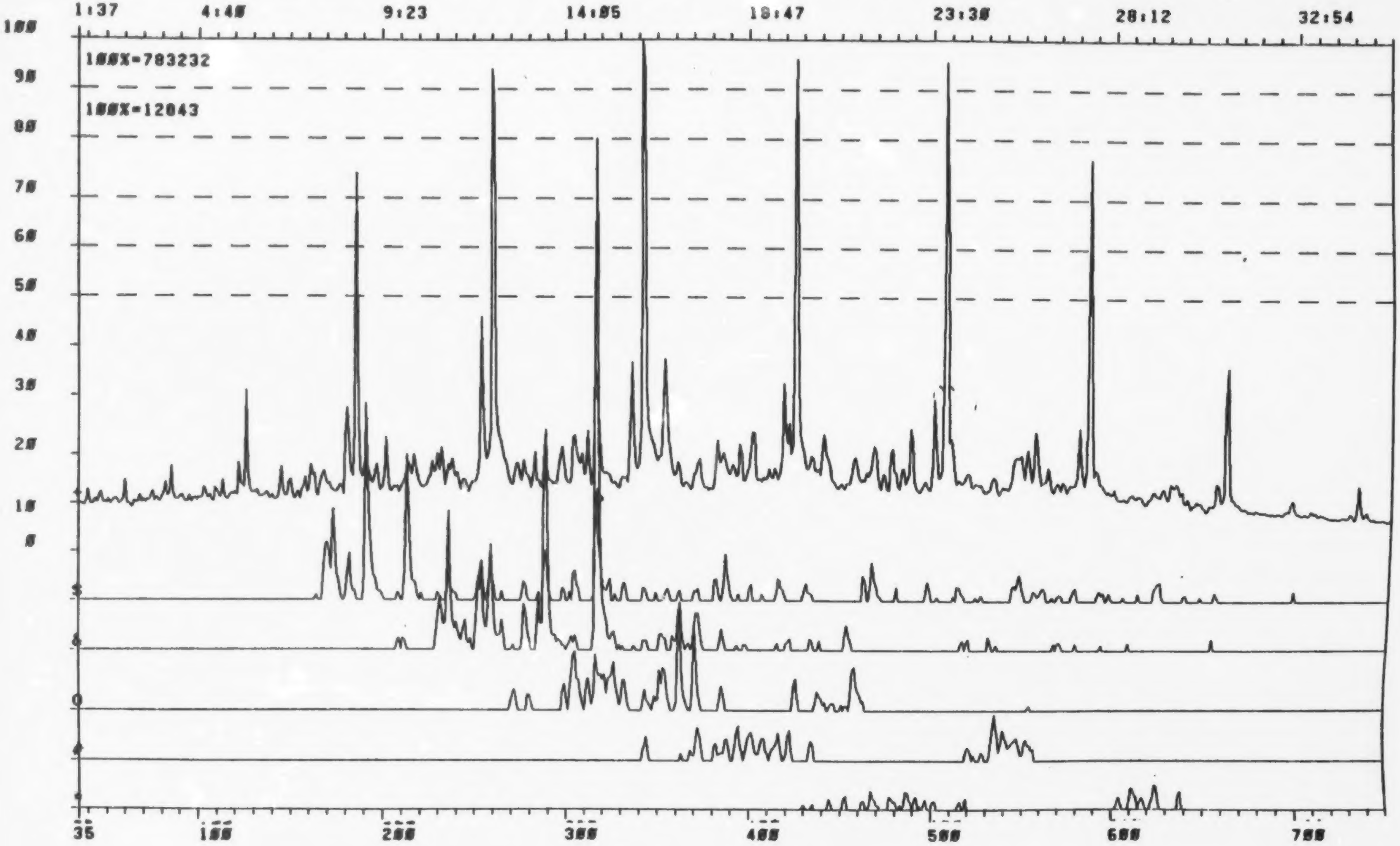
* 174 # 160 O 146 & 132 + TIC (-8)



GC CROSS SCAN REPORT, RUN: 3F1050

7 COMPOSITE EDM. COKER DIST 162-277C 261-85-65³ 060304

* 176 # 162 O 148 & 134 $ 120 + TIC (-6, -105)



APPENDIX III

Department of Chemistry

University of Toronto TORONTO ONTARIO M5S 1A1

May 30, 1986

H. Notzl
Petro-Canada
2489 North Sheridan Way
Mississauga, Ontario
L5K 1A8

Dear H. Notzl:

Enclosed are the ^{1}N NMR spectra of the middle distillate samples. The spectra were recorded on a Varian XL-400 spectrometer according to the methods outlined on the page entitled 'Experimental Procedures'. Table 1 summarizes the relative composition of each sample and the numbers represent the percentage of the integrated intensity of each component relative to the total integrated intensity of the sample. Also enclosed is a photocopy of the charges which will be sent to you from the chemistry department.

The data in Table 1 were obtained as follows. In the ^{1}H spectra a specific chemical shift range was assigned to each proton type in a manner similar to that shown in reference 1: aromatic 6.00 - 8.10 ppm; olefinic: 4.40 - 6.00 ppm; α-alkyl: 1.45 - 3.50 ppm; CH_2: 1.05 - 1.45 ppm; CH_3: 0.5 - 1.05 ppm. The term α-alkyl refers to saturated alkyl protons adjacent to either aromatic or olefinic groups. Saturated methylene and methyl protons are designated by CH_2 and CH_3, respectively. In samples AP4(SC), AP5(SC), and AP7(SC) the toluene CH_3 was used to determine the relative concentration of toluene which appeared to be the only aromatic component present. The ethanol concentration in the hydroborated samples HB1B, HB4B, and HB6B was determined from the methylene quartet since the CH_3 triplet was overlapped with the saturated CH_2 signals. Samples HB1B, HB6B, and HB7B contained other signals in the ethanol methylene region. These signals were assumed to be from other alcohols and their integrated intensity was added to that of ethanol to give the total alcohol entry in Table 1. The numbers were derived by measuring the integral for each region and the integral was adjusted to the integral scale (IS value written on the expansions) corresponding to the saturate region from 0.5 - 3.5 ppm. For example, in AP1 the aromatic integral was measured as 4.18 cm at IS=400. This is equivalent to an integral of 0.418 at IS=40 which was used for the saturate proton region. The total saturate component in these samples may be obtained from the sum of the CH_2 and CH_3 percentages.

Lash Miller Chemical Laboratories 80 St. George Street Telephone (416) 978-3566

There are a number of problems associated with quantitative analysis by NMR (see references 2-4) which make the data in Table 1 not very accurate when compared with GCMS which can separate and identify individual compounds. This results from the overlap of signals in the ^{1}H spectra which makes it difficult to acccurately identify and integrate resonances of a single component or a class of compounds. Evidence of this occurs in the α-alkyl region which contains signals from alkyl substitutents on aromatic and olefinic groups as well as from the iso-paraffin compounds. Since signal overlap made it difficult to distinguish the iso-paraffin from the n-paraffin resonances this ratio was not calculated. This problem of signal overlap should be kept in mind if attempting the data analysis methods presented in reference 1.

Carbon-13 NMR can alleviate the above problem to a certain degree, however, there is still an overwhelming number of aliphatic carbon resonances compressed in a 30-40 ppm range. The carbon signals can be differentiated by the use of various multiplicity sorting pulse sequences such as the attached proton test (APT)(5). The remaining problem is then to assign the carbon signals to a specific compound. Quantitative measurements from ^{13}C spectra requires the suppression of the nuclear overhauser enhancement (nOe) and the addition of paramagnetic compounds such as $Cr(accac)_3$ to enhance the relaxation of the ^{13}C nuclei (2,3). An attempt was made to determine the relative ethanol concentration in HB6B using the overhauser suppression method. In the absence of $Cr\ (acac)_3$, long delay times are required between pulses to ensure complete relaxation of the ^{13}C nuclei and suppression of the nOe. This makes it difficult to achieve a good signal/noise (S/N) ratio in a reasonable period of time. After about 2 hours of acquisition the ethanol region of HB6B still had a poor S/N ratio resulting in a very inaccurate integral. A two or three fold increase in sample concentration would be required to overcome this problem.

To summarize, ^{1}H NMR serves a general guide to the relative concentrations of the components in the distillation samples. Signal overlap, however, reduces the accuracy of this data. Carbon-13 NMR may used as an alternative method provided the procedures outlined above are followed and the carbon resonances can be correctly assigned.

Sincerly yours,

Donald W. Hughes

Donald W. Hughes

DWH/11

REFERENCES

1. D.R. Clutter, L. Petrakis, R.L. Stenger, Jr., and R.K. Jensen Anal. Chem. 44, 1395 (1972).

2. J.N. Shoolery, Prog. NMR Spectrosc. 11, 79 (1977).

3. D.E. Leyden and R.H. Cox, Analytical applications of NMR J. Wiley and Sons, New York 1977.

4. E.D. Becker, High resolution NMR 2nd Edition, Academic Press, New York 1980.

5. S.L. Patt and J.N. Schoolery, J. Magn. Reson. 46, 535 (1982).

EXPERIMENTAL PROCEDURES

Proton NMR spectra were recorded at 399.869 MHz on a varian XL-400 spectrometer. The spectra were acquired in 32-64 scans over a sweep width of 4000 Hz (3.752 s acquisition time). Spectra were acquired in 32K data points and a 1.0 s delay was used between each acquisition. The free induction decays were processed without the application of any weighting functions and were zero-filled to 64K.

Carbon-13 spectra were obtained at 100.559 MHz. The spectra were recorded over a 20.0 KHz sweep width in 32K data points (0.750 s acquisition time) a 1.0 s delay was used between each acquisition. The spectra were acquired in 500-1500 scans. The data were processed with the application of an exponential weighting function producing a 1.0 Hz line broadening and were zero-filled to 64K.

Samples were dissolved in $CDCl_3$ (MSD Isotopes) with the petroleum fraction constituting approximately 20% of the total sample volume. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS) which was used as internal reference.

TABLE 1. Relative Composition of middle distillate samples

Protons	AP1	AP2	AP3	AP4	AP5	AP6	AP7
Aromatic	5.5	4.3	3.4	6.8	4.4	7.1	4.5
Olefinic	2.0					0.7	2.5
α-Alkyl	26.1	22.2	23.8	35.8	14.5	23.0	24.5
CH_2	35.7	38.7	35.0	30.1	45.0	34.4	44.7
CH_3	30.7	34.8	37.8	27.3	36.1	34.8	23.8

	AP1(SC)	AP2(SC)	AP3(SC)	AP4(SC)	AP5(SC)	AP6(SC)	AP7(SC)
Aromatic	0.3	0.2	1.0			1.1	
Olefinic	1.9					1.1	2.4
Toluene CH_3				1.3	0.7		2.3
α-Alkyl	17.6	12.9	20.0	31.6	11.3	13.8	14.5
CH_2	40.1	44.4	39.0	34.5	50.4	39.9	50.2
CH_3	40.1	42.5	40.0	32.6	37.6	44.1	30.6

	HB1B	HB2B	HB3B	HB4B	HB5B	HB6B	HB7B
Aromatic	5.1	2.7	4.0	6.7	4.5	6.3	3.6
Olefinic							
EtOH CH_2	0.3			2.1		0.5	
Total Alcohol	0.7					0.7	1.0
α-Alkyl	20.8	19.5	22.8	37.2	14.9	27.3	18.4
CH_2	36.5	41.3	34.6	27.5	45.0	29.9	51.9
CH_3	36.9	36.5	38.6	26.5	35.6	35.3	31.1

①

H NMR SPECTRA
AP1 - AP7

AFI SUNCOR COKER 21-4-8

CDCl3

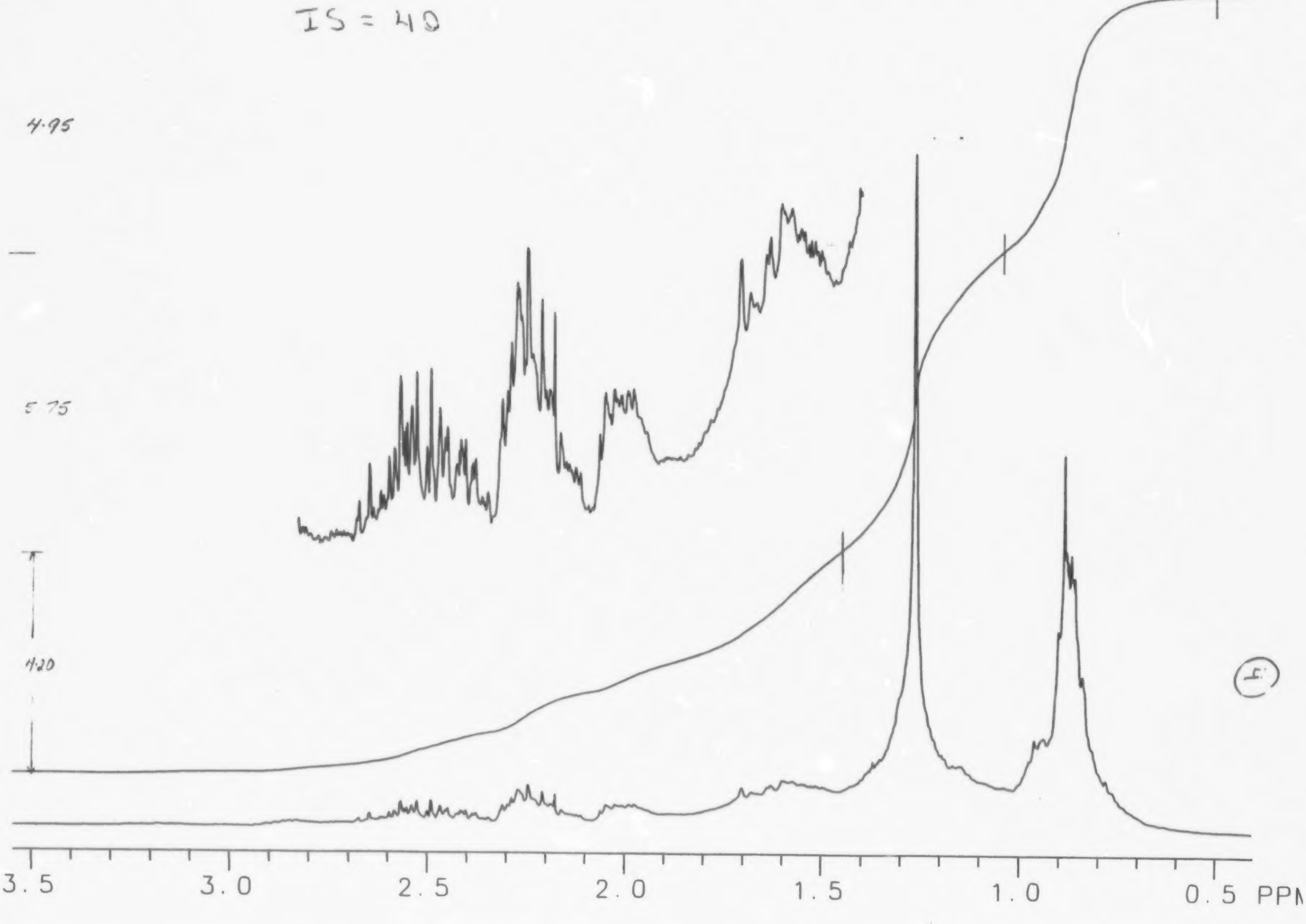
```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   46.27
 RFL=    66.4  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01  2320.17    5.802   47.762
 02  2313.30    5.785   48.711
 03  2160.83    5.404   51.065
 04  2160.13    5.402   74.319
 05  2159.15    5.400   62.531
 06  2156.81    5.394   55.250
 07  2156.05    5.392   63.226
 08  2155.04    5.389   55.860
 09  2153.78    5.386   48.874
 10  2150.80    5.379   48.084
 11  2000.65    5.003   63.333
 12  1999.97    5.002   58.280
 13  1999.14    4.999   55.848
 14  1998.60    4.998   68.605
 15  1983.56    4.961   65.973
 16  1982.88    4.959   60.243
 17  1982.06    4.957   60.352
 18  1981.53    4.955   73.871
 19  1979.80    4.951   53.157
 20  1971.67    4.931   63.271
 21  1970.52    4.928   57.989
 22  1969.30    4.925   56.428
 23  1961.37    4.905   65.080
 24  1960.39    4.903   58.309
 25  1959.11    4.899   59.996
 26  1872.13    4.682   47.161
 27  1871.61    4.681   48.552
 28  1871.18    4.679   46.756
 29  1863.10    4.659   46.380
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   46.27
  RFL=    66.4  RFP=        0

INDEX  FREQ     PPM   INTENSITY
 01   503.28   1.259  130.685
 02   352.09   0.881   72.702
 03   349.72   0.875   54.311
 04   348.13   0.871   52.229
 05   344.95   0.863   53.552
 06   343.12   0.858   49.138
 07   341.56   0.854   49.139
```

```
  ACQUISITION                                            PROCESSING
SFRQ   399.869         DATE  21-04-86             SE    NOT USED
TN       1.750         SOLVNT  CDCL3              LB    NOT USED
SW      4000.0         FILE    H                  RE    NOT USED
AT       3.752                                    CD    NOT USED
NP       30016            DECOUPLING              CCD   NOT USED
FB        2200         DN          1.750          AF    NOT USED
BS          16         DO           74.5          FN       65536
SS           0         DM          NNN            MATH     F
PW         1.0         DLP            20
P1           0                                       SPECIAL
D1       1.000               FLAGS                TEMP  NOT USED
D2           0         IL         N               VTC       25.0
TO           0         IN         N               PW90      13.0
NT          32         DP         Y
CT          32
```

IS = 40

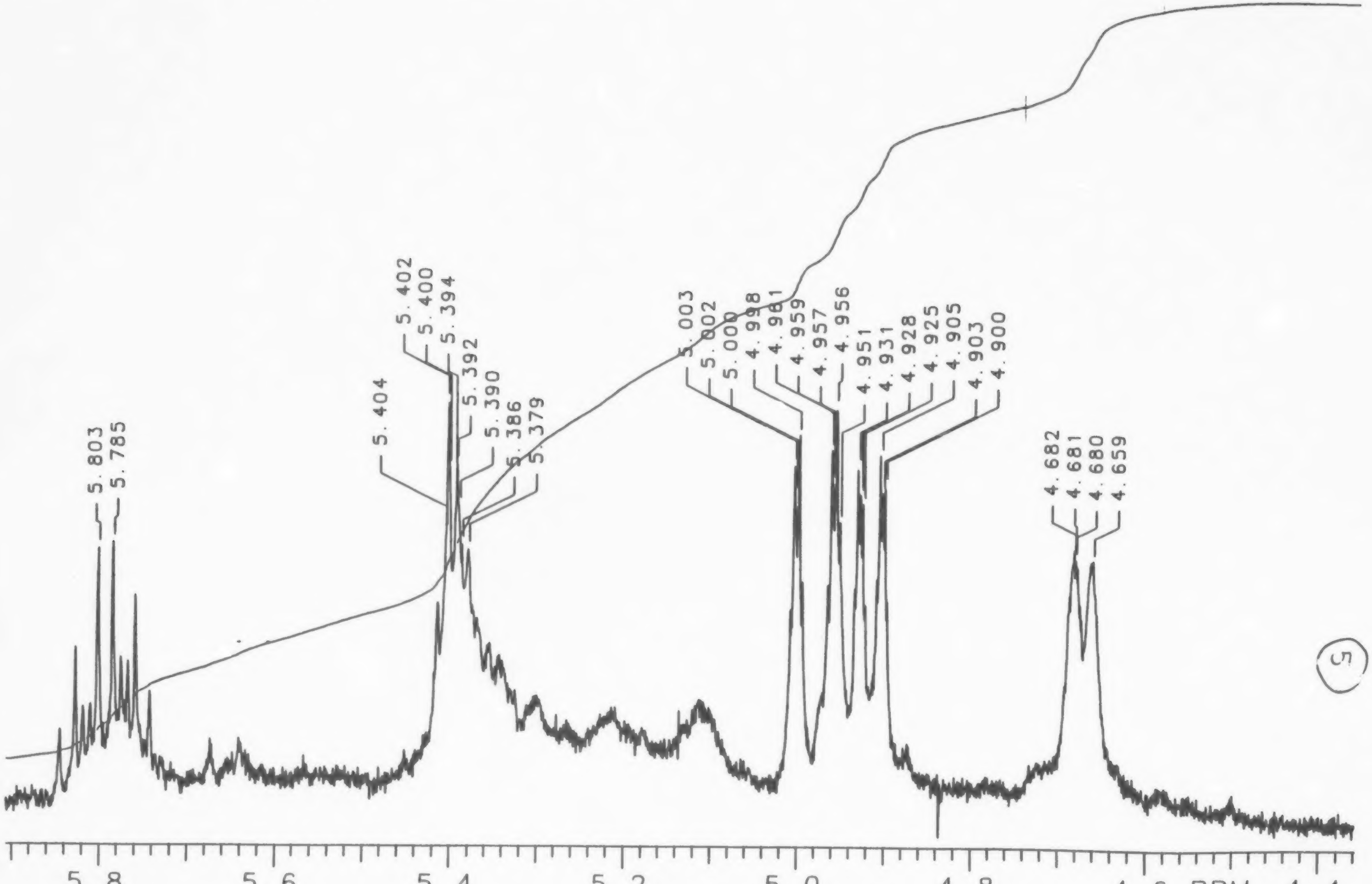
API SUNCOR COKER
$CDCl_3$
IS = 40



④

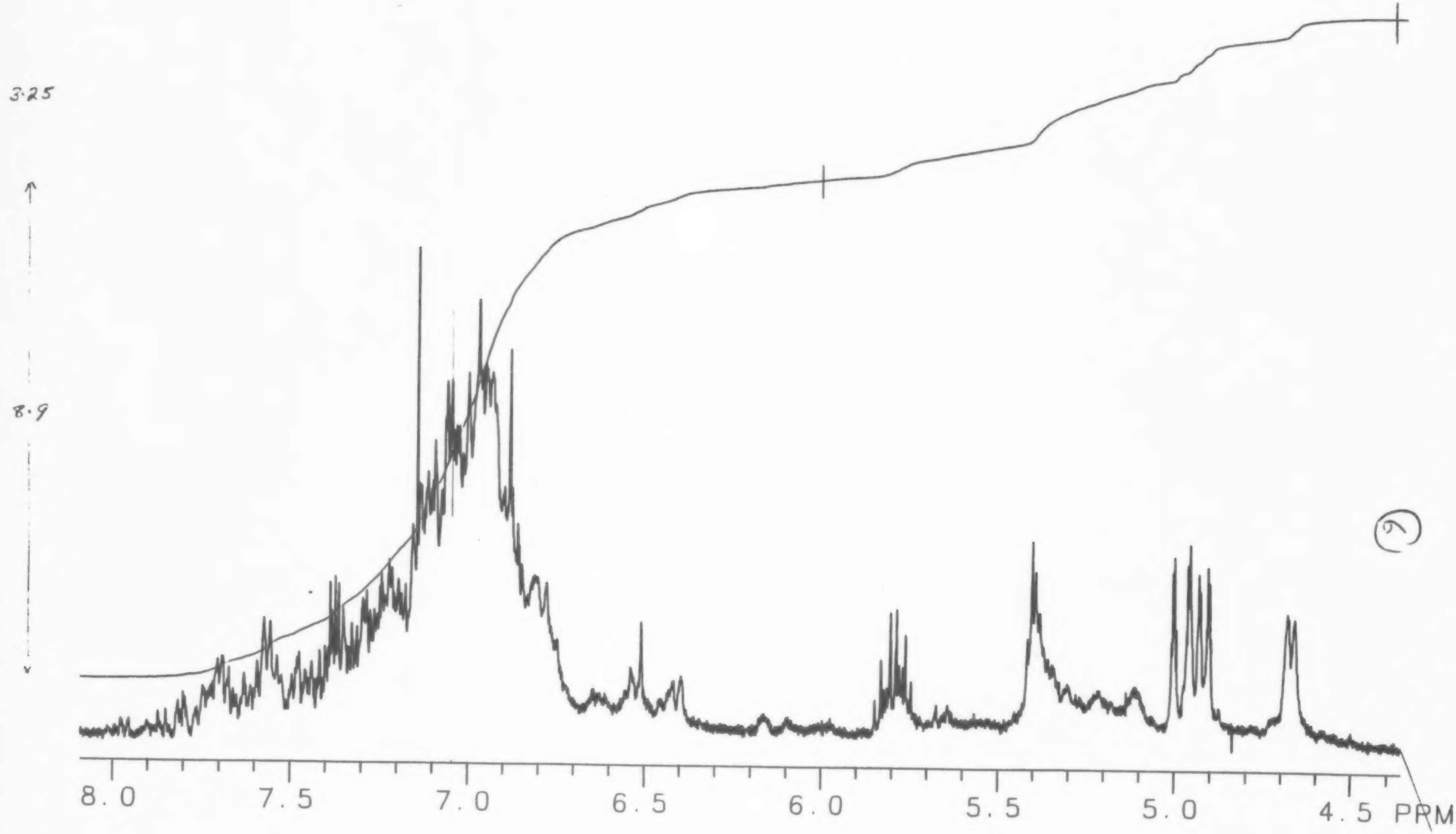
IS = 1800

API SUNCOR COKER
$CDCl_3$
IS = 1800

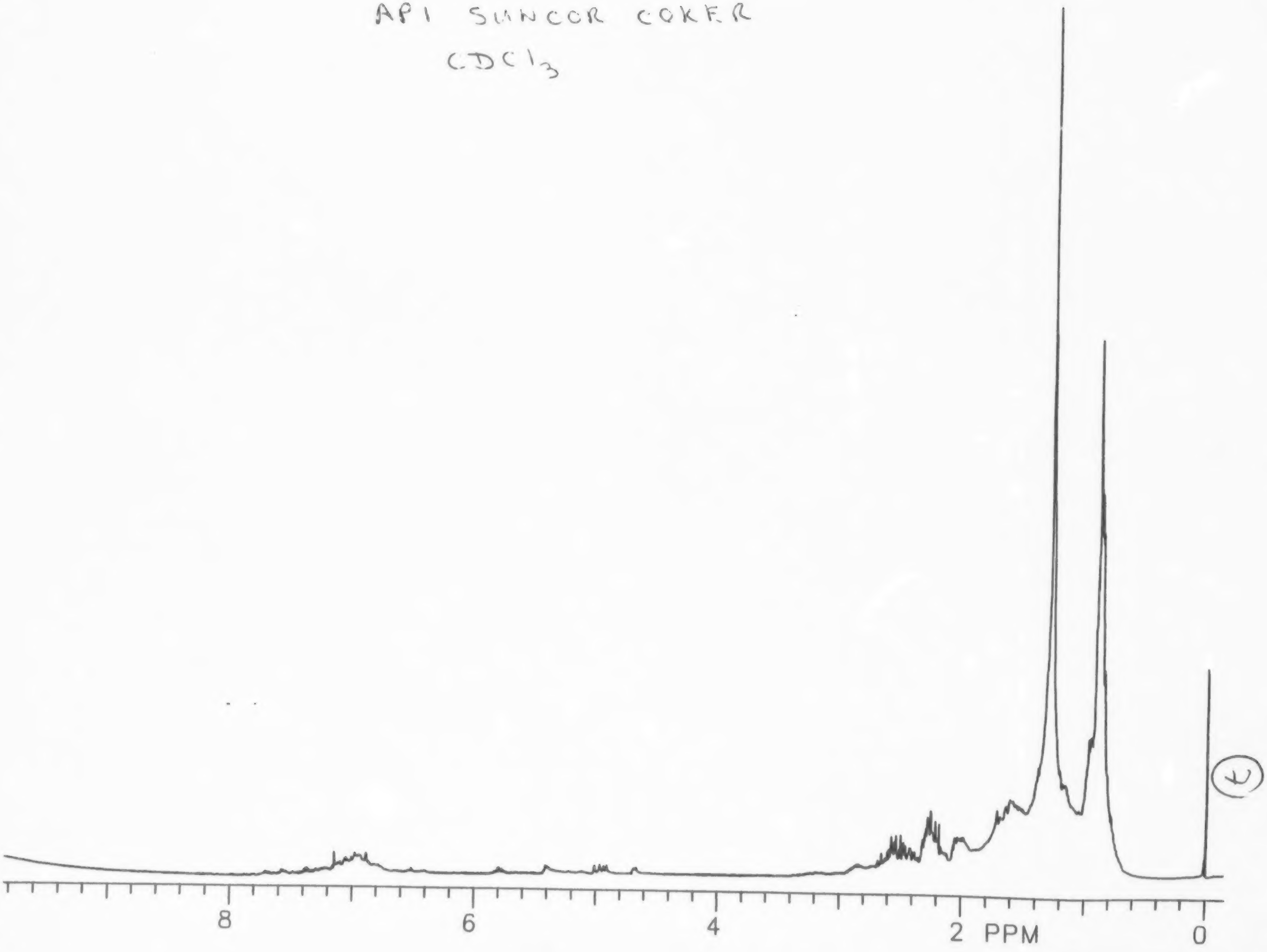


⑤

API SUNCOR COKER
CDCl$_3$



API SUNCOR COKER
CDCl$_3$



⑧

AP2 .SUNCOR HT 21-4-86

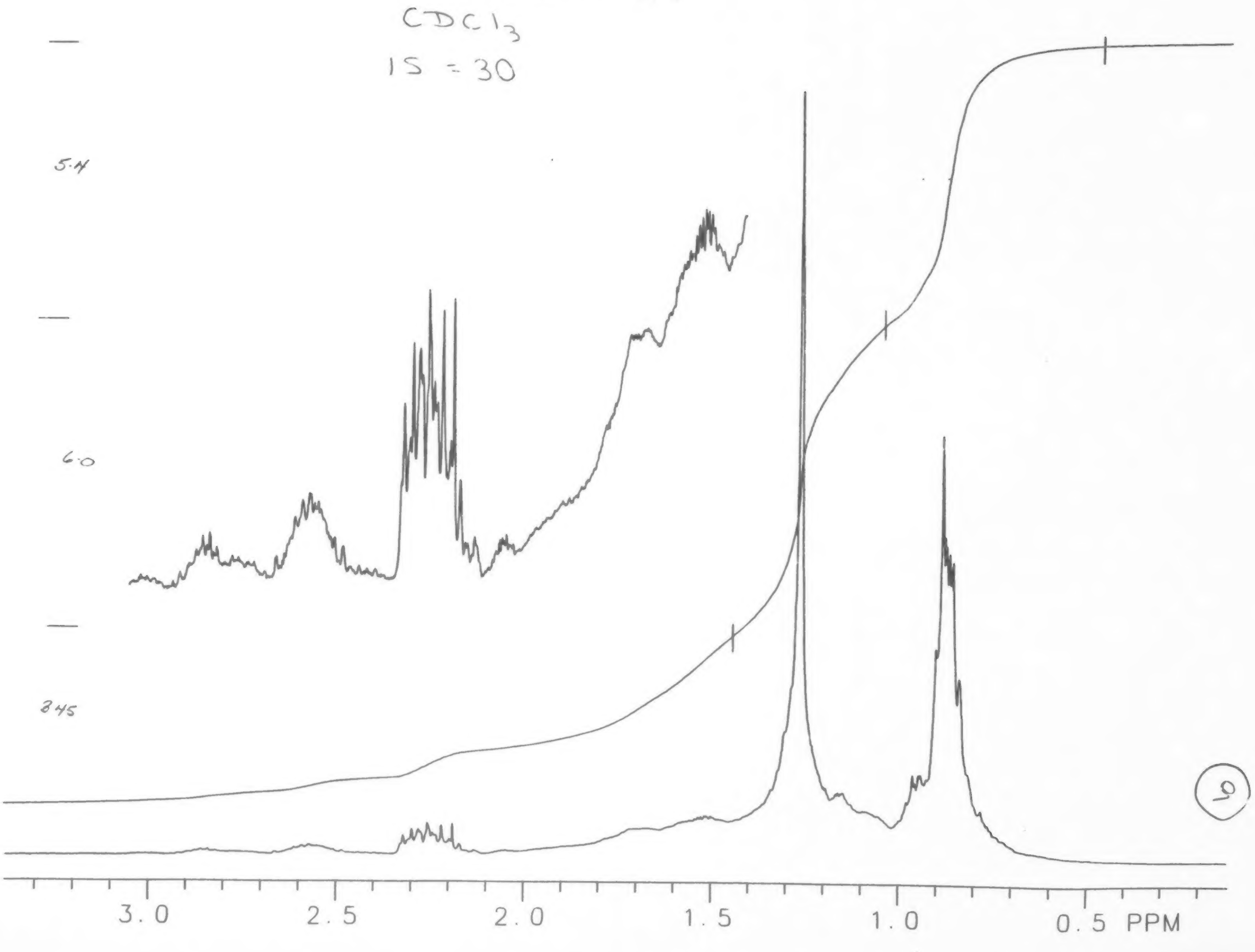
$CDCl_3$

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   33.31
  RFL=   243.7  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01    512.93    1.283   34.104
 02    504.17    1.261  150.494
 03    358.93    0.898   41.762
 04    352.31    0.881   83.295
 05    350.01    0.875   63.572
 06    348.28    0.871   61.708
 07    345.20    0.863   60.392
 08    343.12    0.858   57.820
 09    341.71    0.855   58.697
 10    334.75    0.837   35.967
 11    333.97    0.835   36.090
```

```
 ACQUISITION                                          PROCESSING
SFRQ   399.869          DATE  21-04-86          SE     NOT USED
TN       1.750          SOLVNT  CDCL3           LB     NOT USED
SW      4000.0          FILE    H               RE     NOT USED
AT       3.752                                  CD     NOT USED
NP       30016             DECOUPLING           CCD    NOT USED
FB        2200          DN          1.750       AF     NOT USED
BS          16          DO           74.5       FN        65536
SS           0          DM          NNN         MATH      F
PW         1.0          DLP           20
P1           0                                     SPECIAL
D1       1.000               FLAGS              TEMP  NOT USED
D2           0          IL          N           VTC        25.0
TO        -200          IN          N           PW90       13.0
NT          32          DP          Y
CT          32
```

S=30

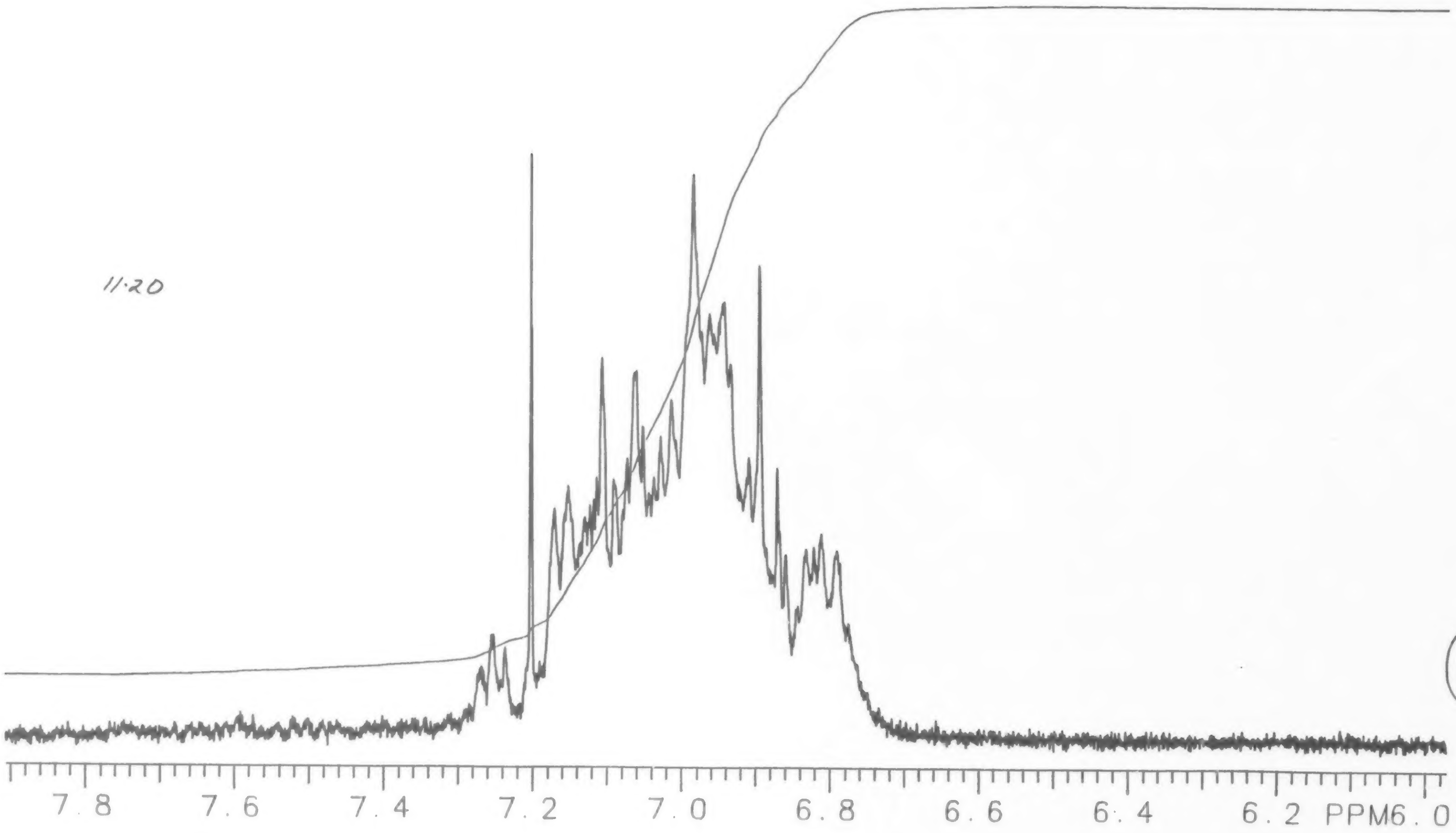
AP2 SUNCOR HT
CDCl$_3$
IS = 30



=500

AP2 SUNCOR HT
$CDCl_3$
IS=500

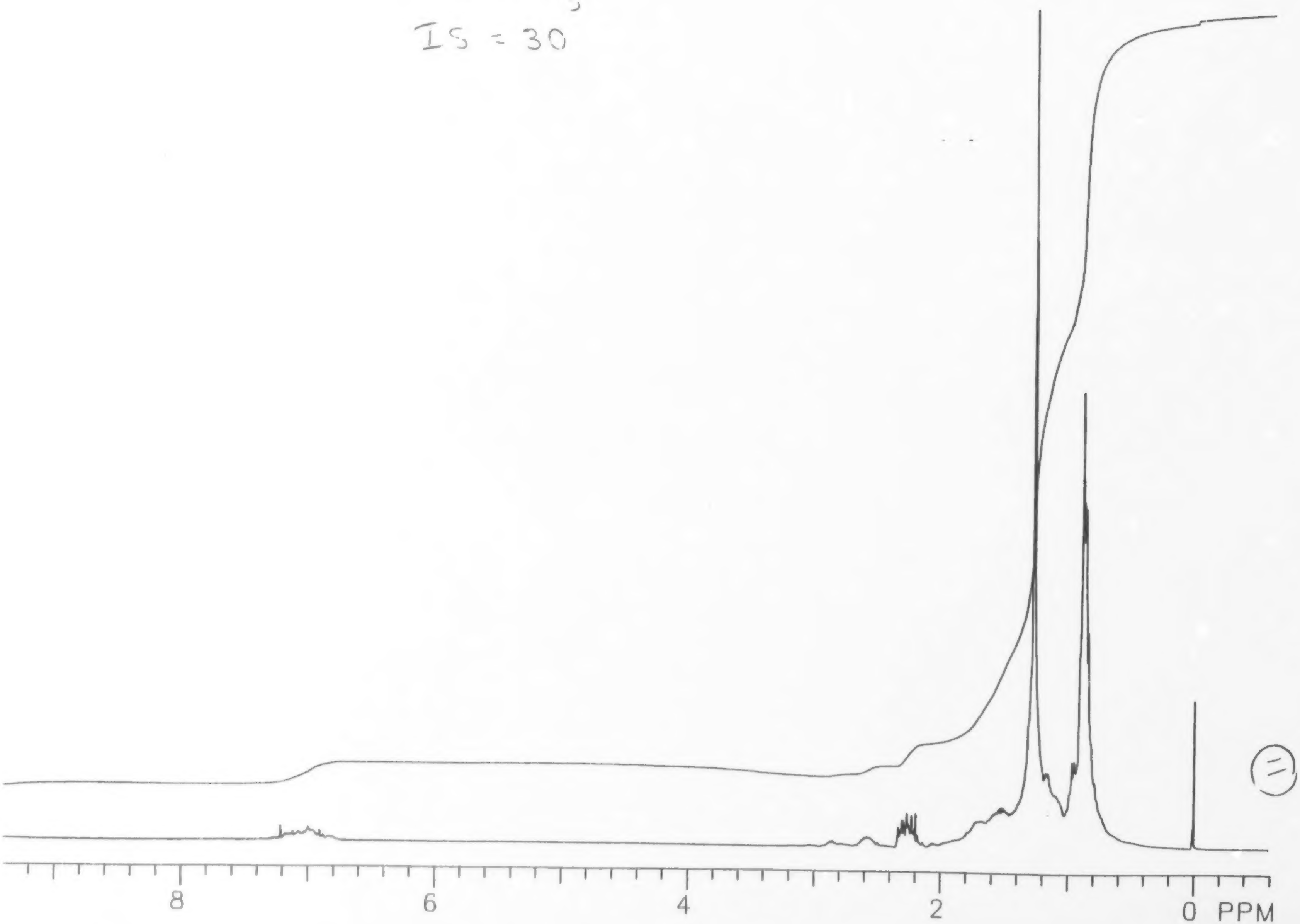
11·20



⑩

IS=30

AP2 SUNCOR HT
$CDCl_3$
IS = 30



⑪

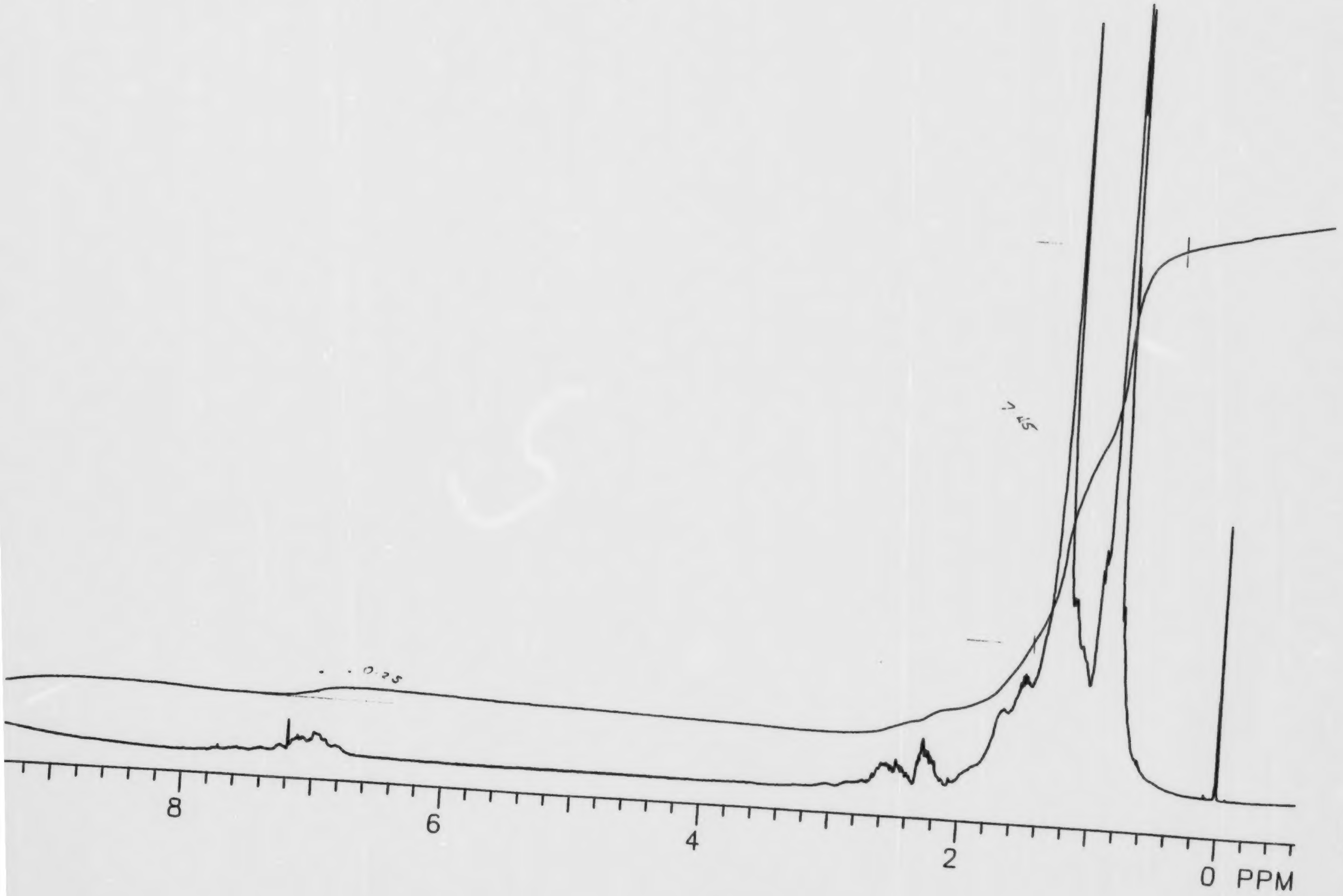
AF3 HUSKY FIREFLOOD 21-4-86

$CDCl_3$

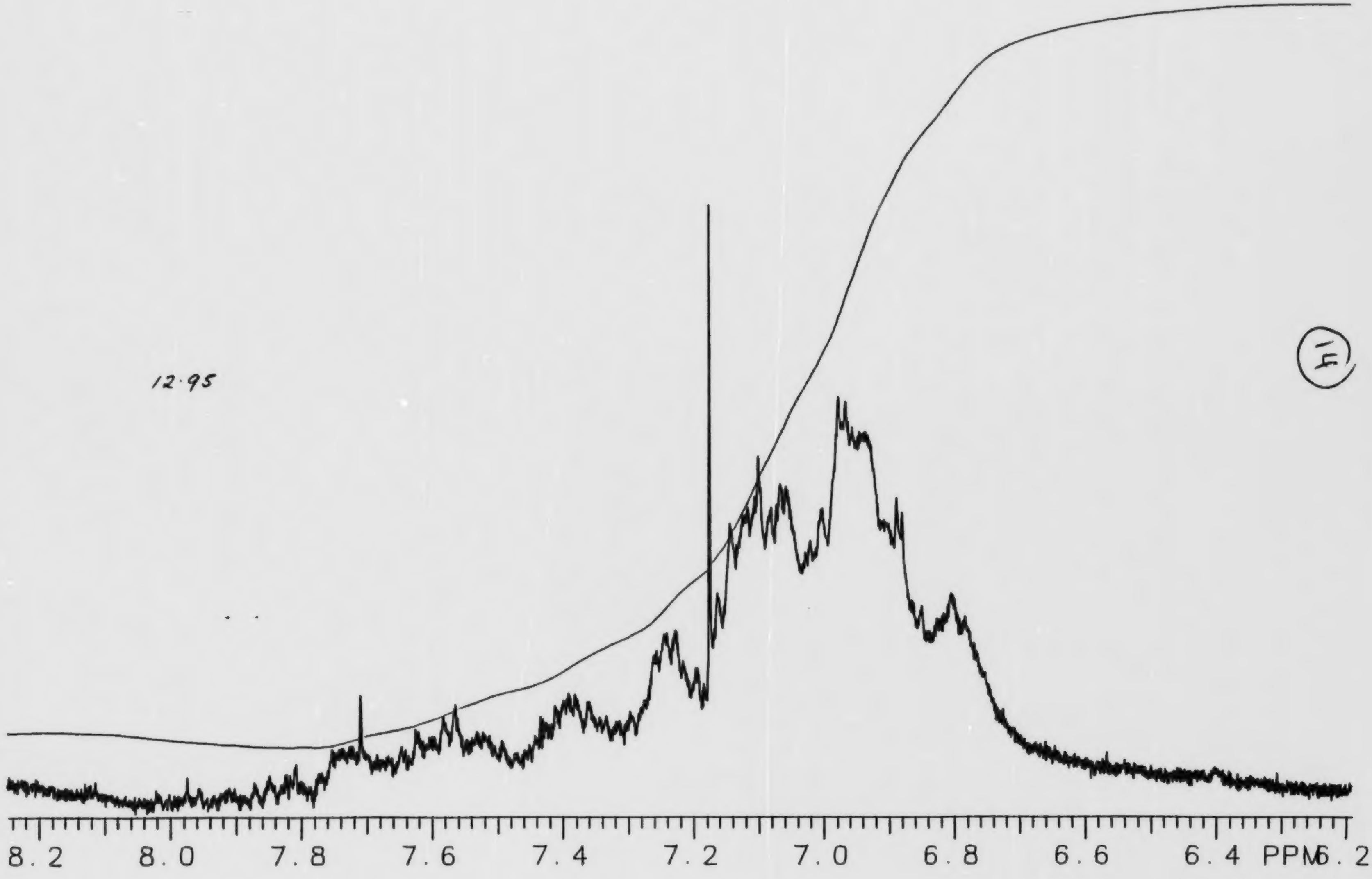
```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   87.62
  RFL=   254.3  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01   503.53    1.259  135.754
 02   351.91    0.880  130.788
 03   350.01    0.875  139.607
 04   348.18    0.871  124.924
 05   345.74    0.865  120.934
 06   345.08    0.863  121.116
 07   343.12    0.858  136.585
 08   341.54    0.854  128.585
 09   335.00    0.838   89.866
```

```
                                                  PROCESSING
  ACQUISITION                             SE      NOT USED
SFRQ   399.869        DATE  21-04-86      LB      NOT USED
TN       1.750        SOLVNT  CDCL3       RE      NOT USED
SW      4000.0        FILE    H           CD      NOT USED
AT       3.752                            CCD     NOT USED
NP       30016           DECOUPLING       AF      NOT USED
FB        2200        DN        1.750     FN         65536
BS          16        DO         74.5     MATH     F
SS           0        DM         NNN
PW         1.0        DLP          20          SPECIAL
P1           0                            TEMP   NOT USED
D1       1.000             FLAGS          VTC         25.0
D2           0        IL         N        PW90        13.0
TO        -200        IN         N
NT          32        DP         Y
CT          32
```

AP3 HUSKY FIREFLOOD
$CDCl_3$



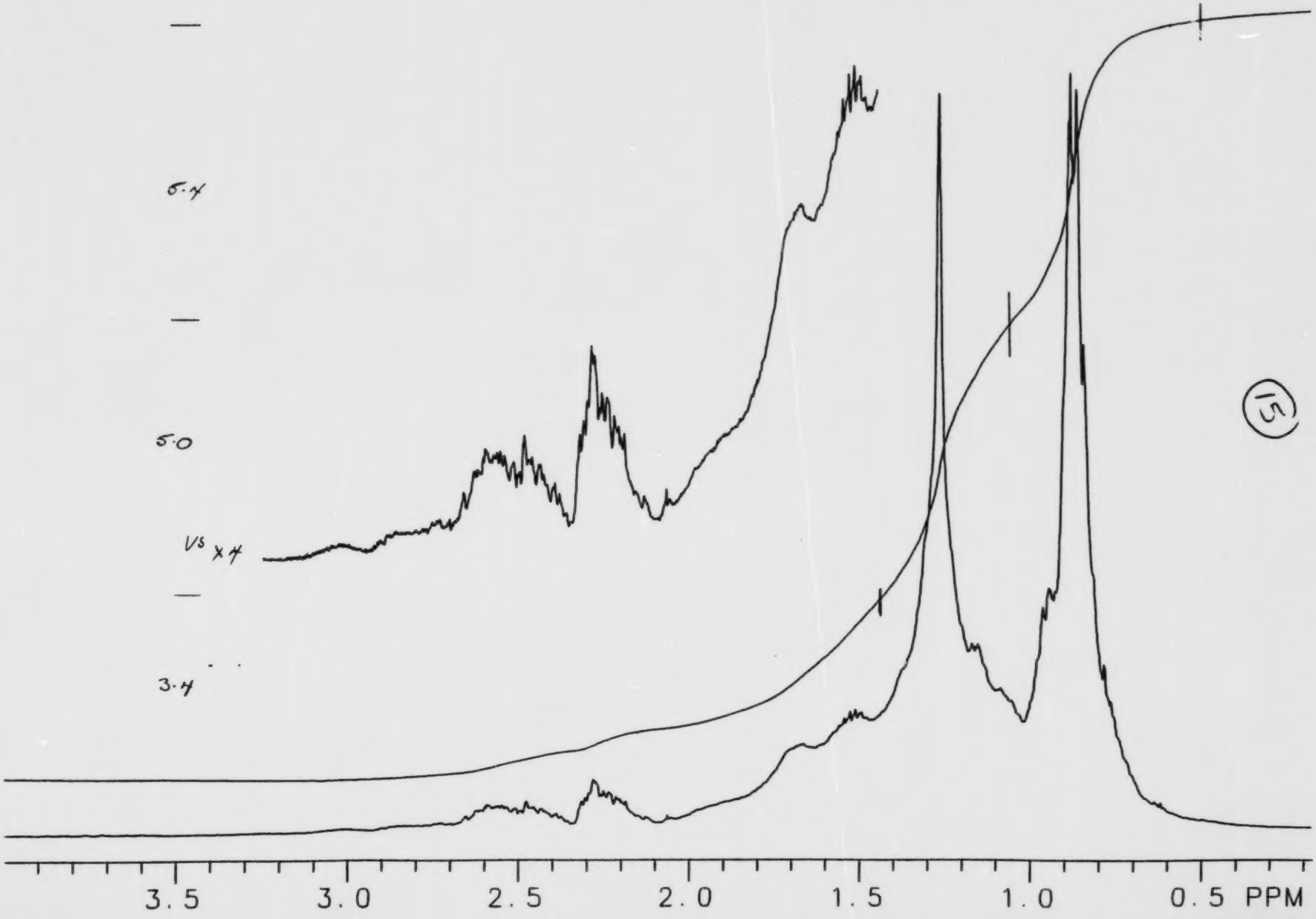
AP3 HUSKY FIREFLOOD
$CDCl_3$
IS = 800



⑭

IS = 30

AP3 HUSKY FIREFLOOD
CDCl$_3$
IS = 30



⑮

AP4 WYODAK 21-4-86

$CDCl_3$

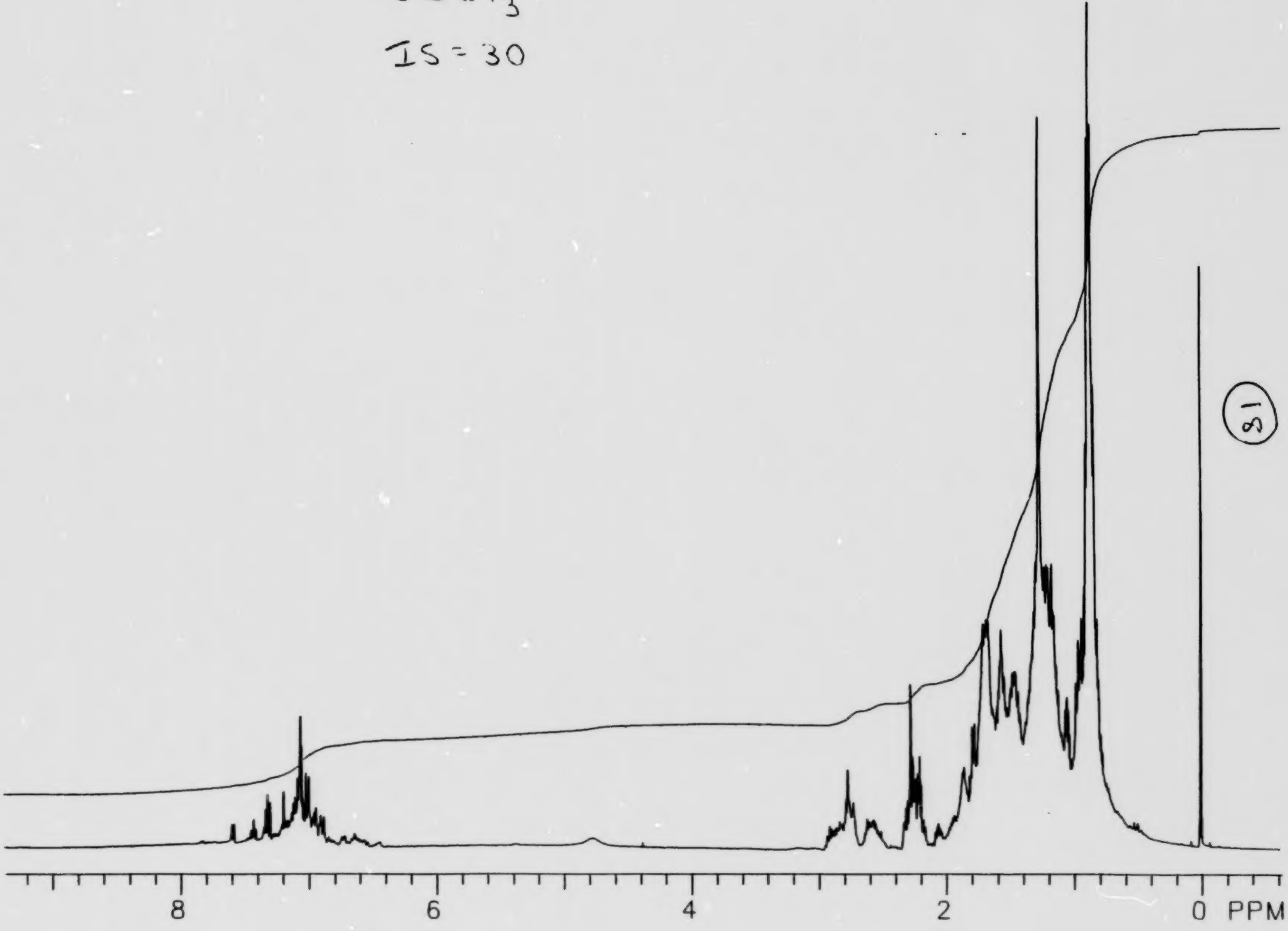
```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   41.81
  RFL=   252.1  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01   2922.21   7.308   50.209
 02   2920.84   7.304   47.439
 03   2913.54   7.286   44.952
 04   2871.06   7.180   53.448
 05   2835.55   7.091   47.685
 06   2828.95   7.075   65.360
 07   2828.24   7.073   67.016
 08   2827.33   7.071   49.230
 09   2826.78   7.069   47.794
 10   2826.11   7.068   44.166
 11   2825.74   7.067   44.605
 12   2824.28   7.063   64.816
 13   2820.79   7.054  111.098
 14   2819.52   7.051  137.349
 15   2817.13   7.045  108.966
 16   2815.03   7.040   52.021
 17   2814.69   7.039   54.614
 18   2812.10   7.033   54.455
 19   2803.77   7.012   43.453
 20   2802.43   7.008   77.671
 21   2801.36   7.006   79.762
 22   2800.62   7.004   57.783
 23   2795.67   6.991   46.897
 24   2794.74   6.989   53.259
 25   2793.80   6.987   74.914
 26   2792.66   6.984   70.309
 27   2770.57   6.929   43.934
 28   2770.11   6.928   43.890
```

⑰

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   52.42
  RFL=   252.1  RFP=       0

INDEX  FREQ     PPM   INTENSITY
 01   516.22   1.291   54.534
 02   515.55   1.289   53.258
 03   513.59   1.284   53.831
 04   512.44   1.282   55.465
 05   511.83   1.280   55.191
 06   510.91   1.278   56.021
 07   508.29   1.271   70.106
 08   504.17   1.261  131.984
 09   358.26   0.896   77.017
 10   354.87   0.887  103.272
 11   352.33   0.881  130.991
 12   349.77   0.875  109.775
 13   348.86   0.872  109.745
 14   347.55   0.869  151.259
 15   345.13   0.863  114.552
 16   343.79   0.860  108.680
 17   342.88   0.857  107.634
 18   341.08   0.853  121.541
 19   340.32   0.851  122.689
 20   336.34   0.841   63.710
 21   334.33   0.836   75.125




                                                       PROCESSING
  ACQUISITION                                       SE    NOT USED
SFRQ   399.869         DATE  21-04-86               LB    NOT USED
TN       1.750         SOLVNT  CDCL3                RE    NOT USED
SW      4000.0         FILE    H                    CD    NOT USED
AT       3.752                                      CCD   NOT USED
NP       30016            DECOUPLING                AF    NOT USED
FB        2200         DN          1.750            FN       65536
BS          16         DO           74.5            MATH      F
SS           0         DM          NNN
PW         1.0         DLP            20                SPECIAL
P1           0                                      TEMP  NOT USED
D1       1.000              FLAGS                   VTC       25.0
D2           0         IL          N                PW90      13.0
TO        -200         IN          N
NT          32         DP          Y
CT          32
```

IS=30

AP4 WYODAK
$CDCl_3$
IS = 30



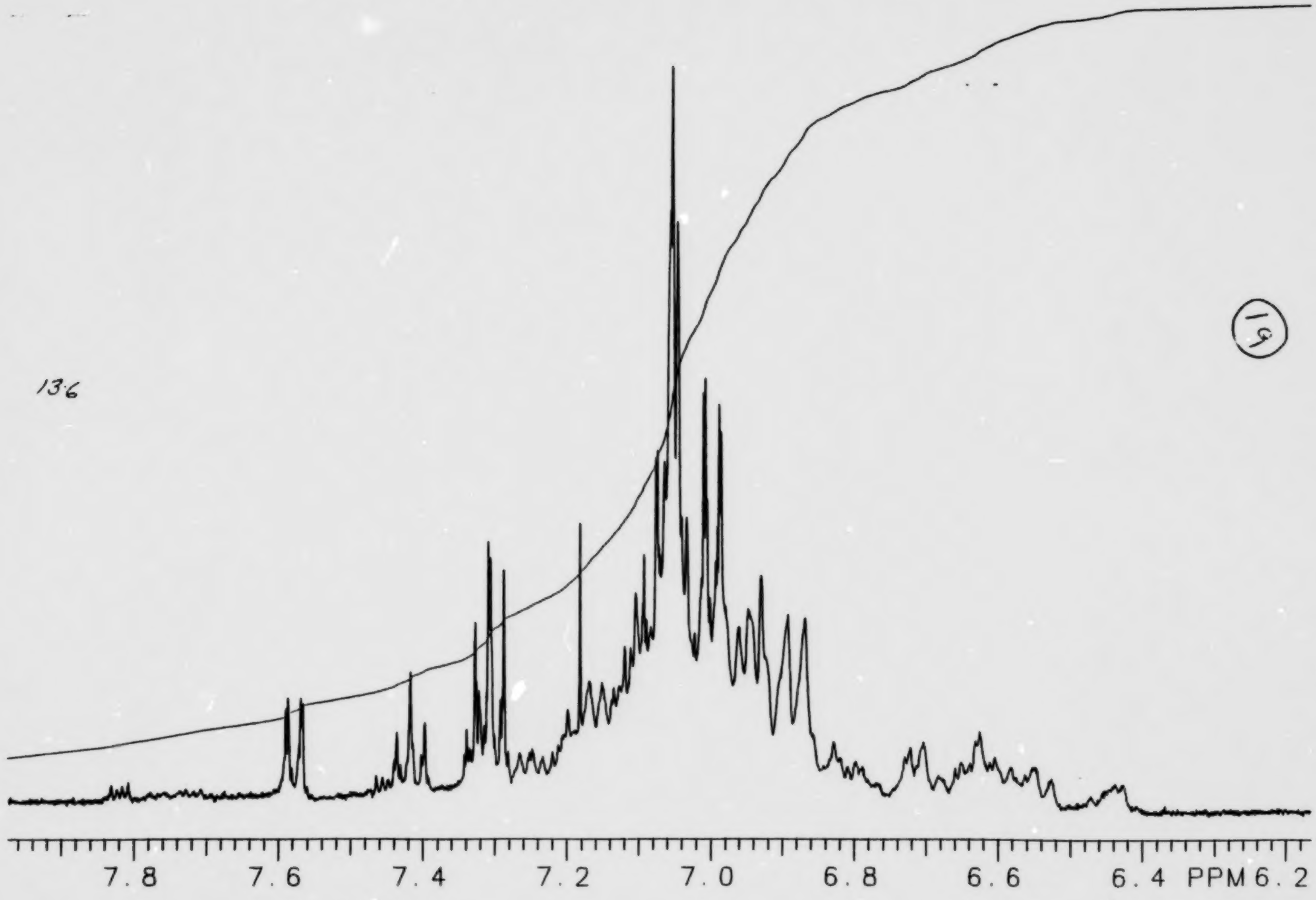
⑱

IS = 500

APH WYODAK

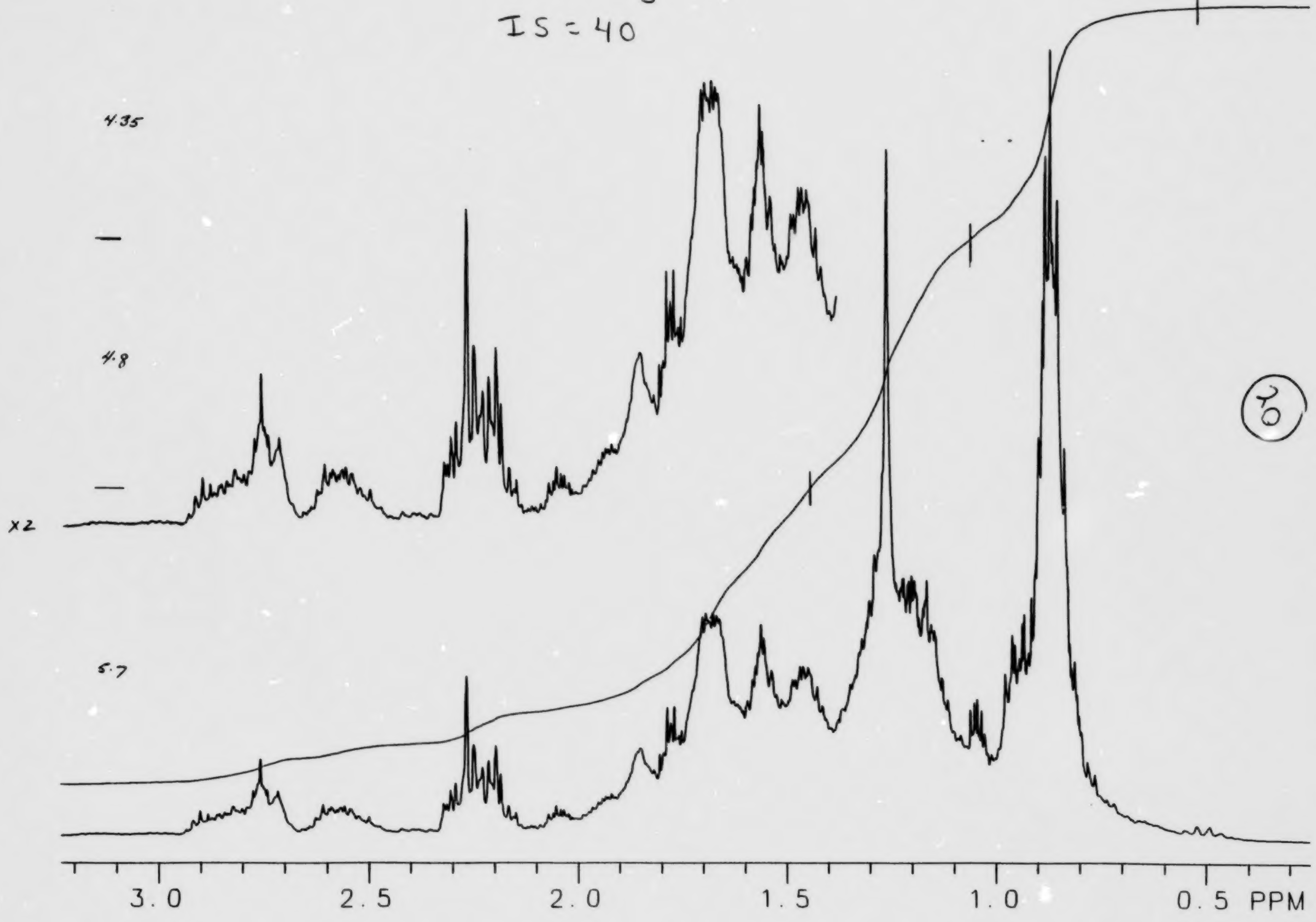
$CDCl_3$

IS = 500



IS=40

APH WYODAK
CDCl$_3$
IS=40



⑳

(21) AP5 COMMERCIAL DIESEL 21-4-86
$CDCl_3$

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   17.74
 RFL=   252.1  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01    519.57   1.299   21.101
 02    511.64   1.280   29.201
 03    503.22   1.258  144.516
 04    494.74   1.237   23.474
 05    490.83   1.227   10.609
 06    489.86   1.225   17.901
 07    358.02   0.895   34.315
 08    356.19   0.891   30.050
 09    351.33   0.879   81.183
 10    349.04   0.873   53.699
 11    347.40   0.869   48.514
 12    344.40   0.861   50.188
 13    342.27   0.856   47.146
 14    340.83   0.852   47.554
 15    333.97   0.835   26.624
 16    333.29   0.833   27.560
 17    332.60   0.832   27.378
 18     -0.98  -0.002   21.016
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   43.86
 RFL=   252.1  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01  2870.93    7.180   90.892
 02  2864.47    7.164   44.999
 03  2857.42    7.146   44.273
 04  2856.78    7.144   45.017
 05  2856.29    7.143   44.851
 06  2839.35    7.101   66.753
 07  2838.01    7.097   51.960
 08  2837.61    7.096   50.219
 09  2827.85    7.072   97.330
 10  2815.76    7.042   53.497
 11  2801.72    7.007   54.580
 12  2801.14    7.005   53.717
 13  2794.03    6.987   75.457
 14  2793.67    6.986   76.593
 15  2793.21    6.985   76.323
 16  2790.28    6.978  130.896
```

22

```
19  2787.96     6.972   66.646
20  2786.49     6.969   53.491
21  2785.70     6.967   56.897
22  2785.12     6.965   55.451
23  2784.48     6.963   51.697
24  2783.81     6.962   50.903
25  2783.20     6.960   48.385
26  2782.83     6.959   47.904
27  2782.53     6.959   46.564
28  2782.10     6.958   45.909
29  2781.73     6.957   44.643
30  2775.87     6.942   62.262
31  2775.26     6.940   65.177
32  2774.62     6.939   64.701
33  2774.11     6.938   64.614
34  2773.55     6.936   63.557
35  2754.60     6.889  110.134
36  2712.37     6.783   44.837
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   28.94
  RFL=   252.1  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01    511.64    1.280   30.670
 02    503.04    1.258  159.457
 03    358.04    0.895   37.004
 04    356.19    0.891   32.423
 05    351.33    0.879   89.110
 06    349.10    0.873   59.173
 07    347.40    0.869   53.627
 08    344.22    0.861   55.492
 09    342.27    0.856   52.334
 10    340.83    0.852   52.979
 11    334.02    0.835   29.856
 12    333.29    0.833   30.969
 13    332.50    0.832   30.840
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   40.39
  RFL=   252.1  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01   919.71    2.300   47.575
 02   915.19    2.289   40.953
 03   910.52    2.277   41.068
```

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```
06   904.51    2.262   71.557
07   903.93    2.261   67.430
08   898.74    2.248  107.658
09   893.12    2.234   50.273
10   892.08    2.233   52.408
11   883.91    2.211   75.604
12   881.16    2.204   52.088
13   871.76    2.180   95.498
14   614.49    1.537   42.953
15   610.98    1.528   43.089
16   607.83    1.520   40.434
17   604.39    1.511   43.911
18   601.19    1.503   46.452
19   597.53    1.494   43.061
20   557.00    1.393   41.356
21   554.92    1.388   43.771
22   554.56    1.387   43.794
23   554.24    1.386   43.729
24   553.63    1.385   44.531
```

```
  ACQUISITION                                    PROCESSING
SFRQ   399.869        DATE  21-04-86          SE    NOT USED
TN       1.750        SOLVNT  CDCL3           LB    NOT USED
SW      4000.0        FILE    H               RE    NOT USED
AT       3.752                                CD    NOT USED
NP       30016           DECOUPLING           CCD   NOT USED
FB        2200        DN          1.750       AF    NOT USED
BS          16        DO           74.5       FN       65536
SS           0        DM          NNN         MATH     F
PW         1.0        DLP            20
P1           0                                  SPECIAL
D1       1.000             FLAGS              TEMP  NOT USED
D2           0        IL          N           VTC       25.0
TO        -200        IN          N           PW90      13.0
NT          32        DP          Y
CT          32
```

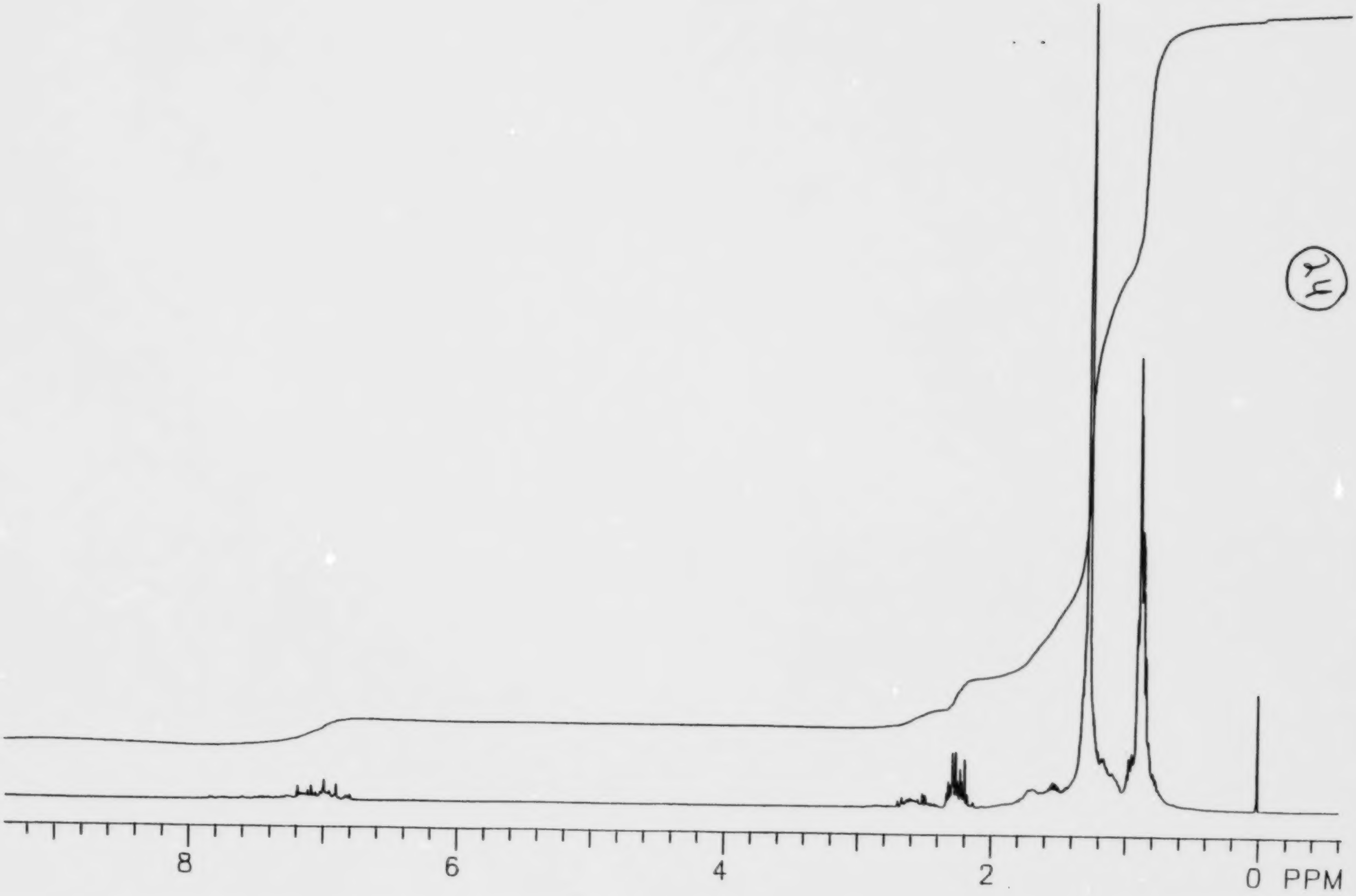
IS=30

APS COMMERCIAL DIESEL

$CDCl_3$

IS = 30

㉔

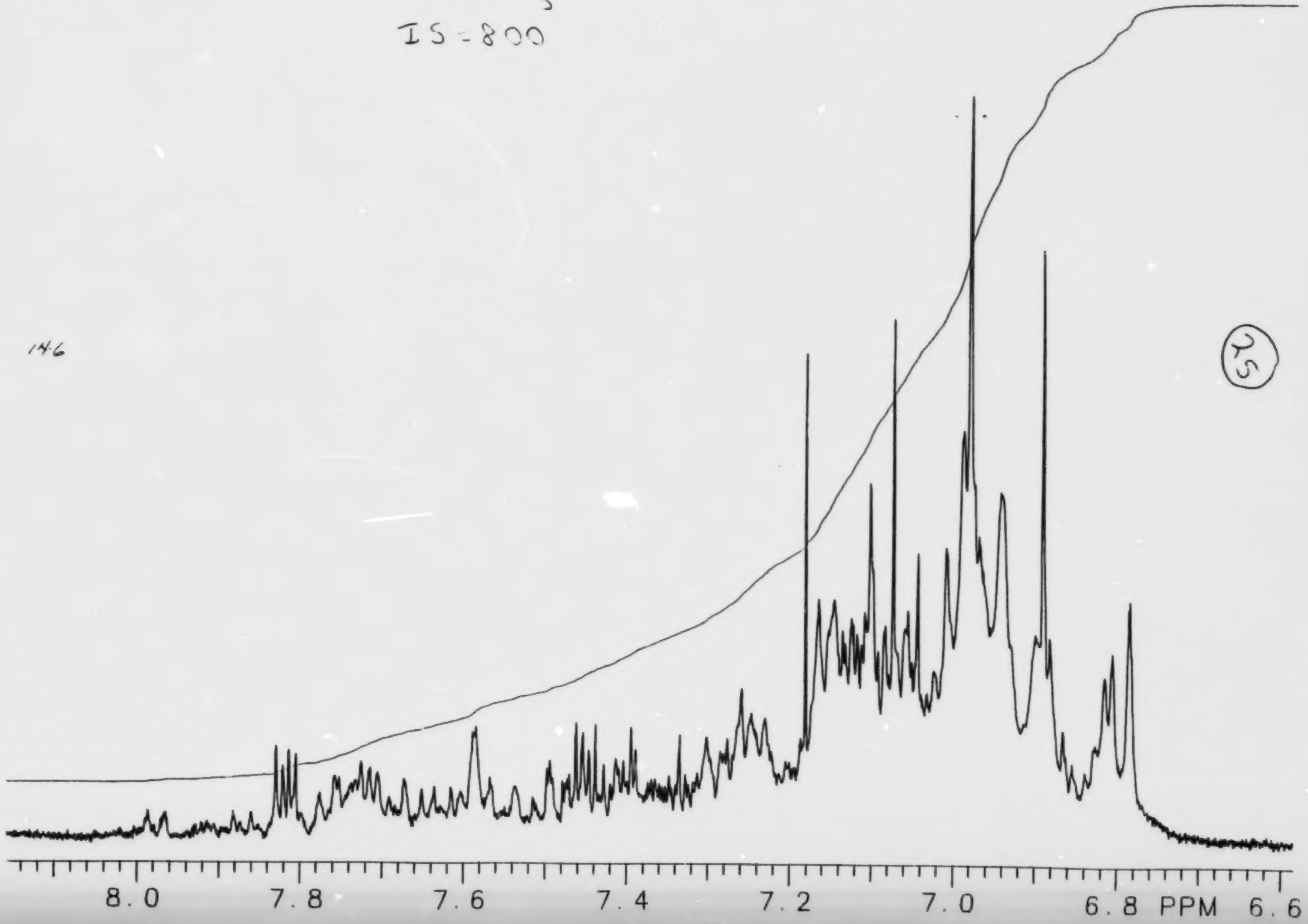


IS=800

APS COMMERCIAL DIESEL
$CDCl_3$
IS=800

146

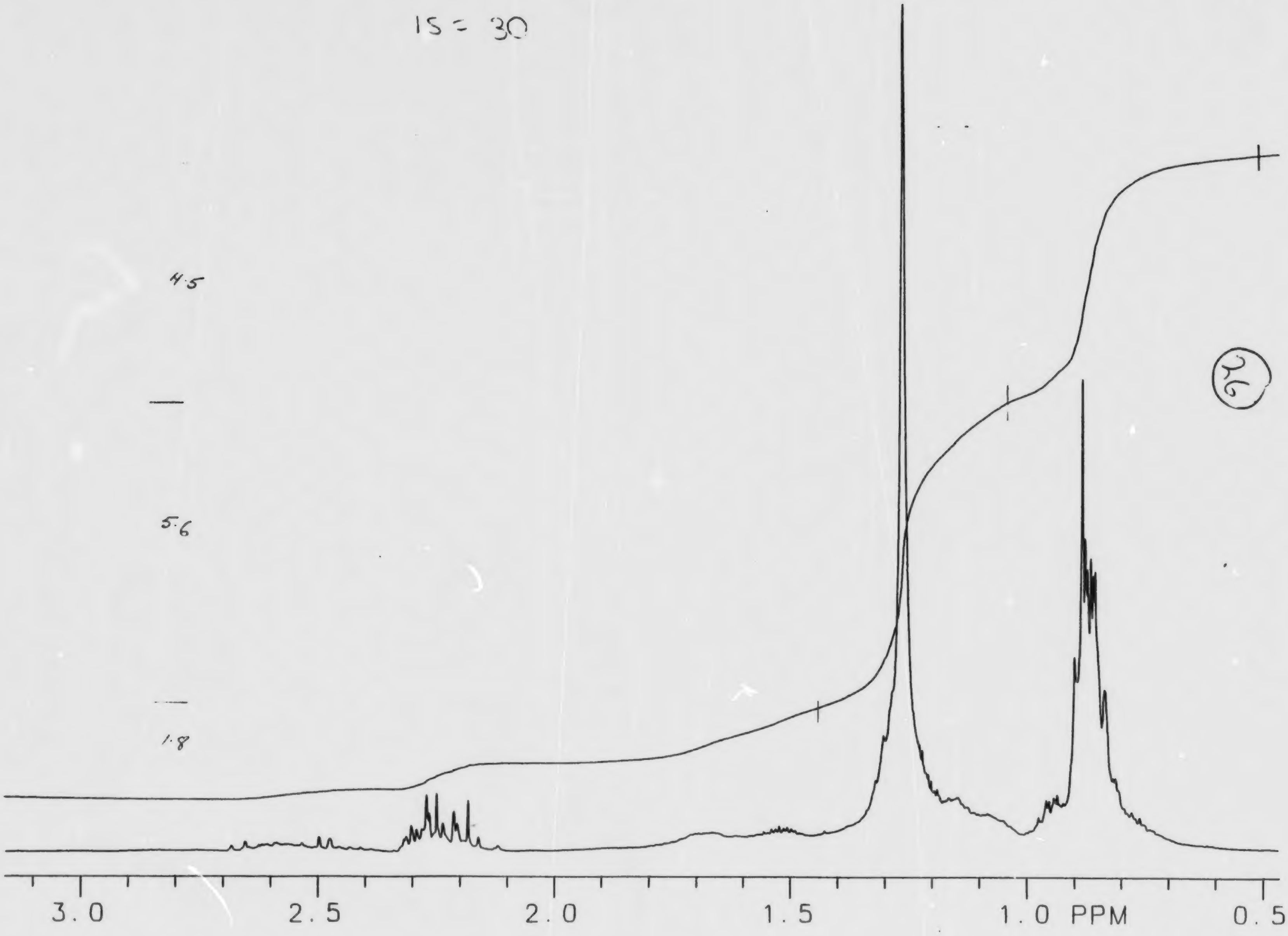
㉕



IS=30

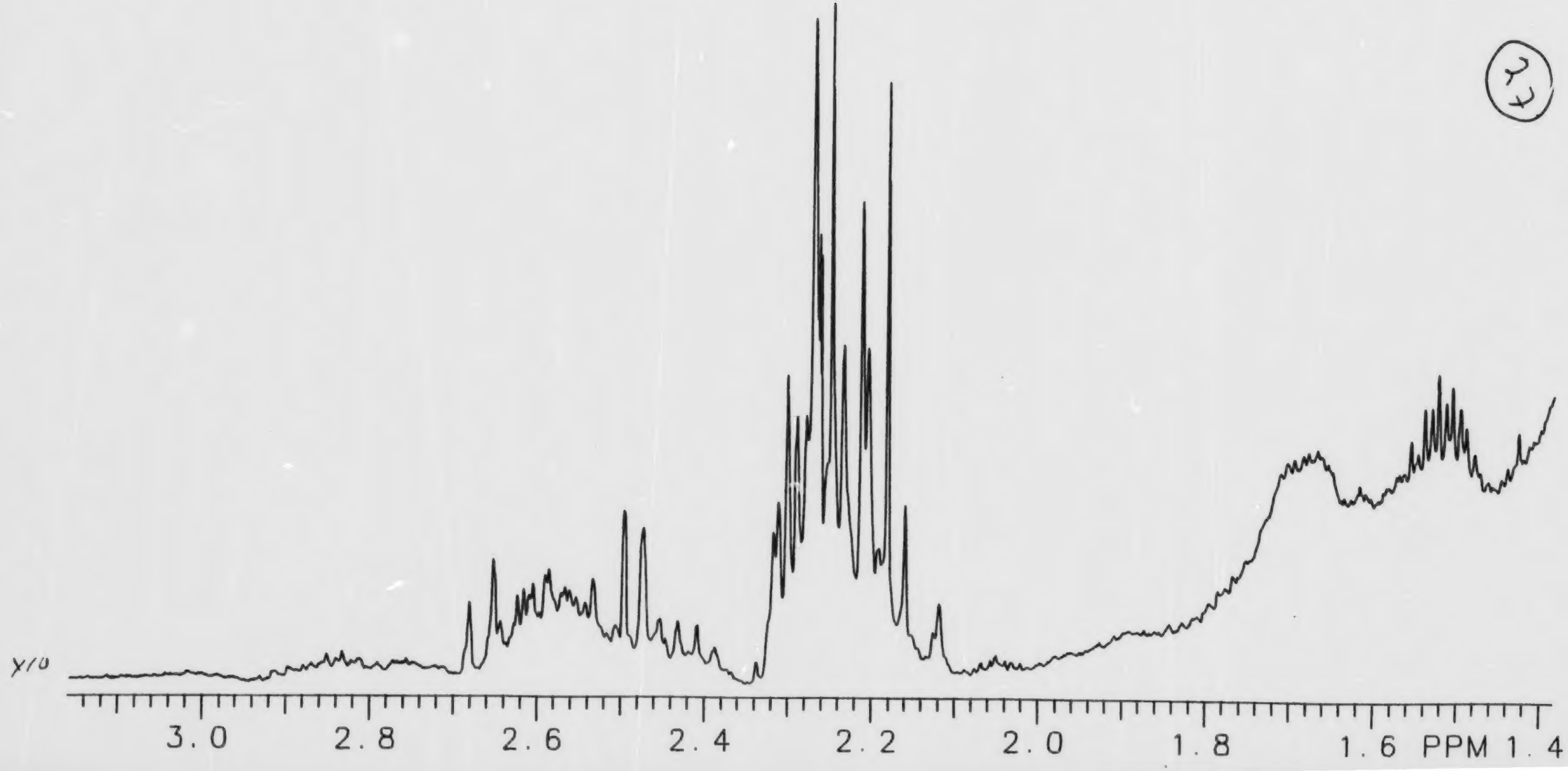
APS COMMERCIAL DIESEL
$CDCl_3$
IS = 30

(26)



APS COMMERCIAL DIESEL
$CDCl_3$

㉗



AP6 SYNCRUDE FFU O/H 21-4-86

CDCl3 ㉘

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   87.62
 RFL=   270.6  RFP=       0

INDEX  FREQ       PPM   INTENSITY
 01   502.00     1.255  149.733
 02   351.48     0.879  130.068
 03   347.64     0.869  115.727
 04   344.34     0.861  118.928
 05     -0.16 -4.07E-4   96.627
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   35.93
 RFL=   270.6  RFP=       0

INDEX  FREQ       PPM   INTENSITY
 01  2319.87     5.802   42.941
 02  2313.06     5.785   43.719
 03  2302.77     5.759   36.645
 04  2002.11     5.007   44.051
 05  2000.55     5.003   66.440
 06  1999.97     5.002   59.462
 07  1999.09     4.999   58.139
 08  1998.45     4.998   66.561
 09  1996.87     4.994   37.016
 10  1985.68     4.966   37.853
 11  1985.17     4.965   46.324
 12  1983.61     4.961   66.719
 13  1982.88     4.959   61.461
 14  1982.02     4.957   62.447
 15  1981.39     4.955   67.924
 16  1980.50     4.953   43.421
 17  1980.19     4.952   43.536
 18  1979.77     4.951   46.524
 19  1972.96     4.934   47.137
 20  1972.47     4.933   47.406
 21  1971.59     4.931   68.432
 22  1970.37     4.928   59.139
 23  1969.54     4.925   54.293
 24  1968.20     4.922   36.338
 25  1962.73     4.908   47.808
 26  1961.49     4.905   63.504
 27  1960.48     4.903   56.106
 28  1960.08     4.902   54.437
 29  1959.29     4.900   51.558
 30  1872.75     4.683   37.501
 31  1872.10     4.682   38.307
```

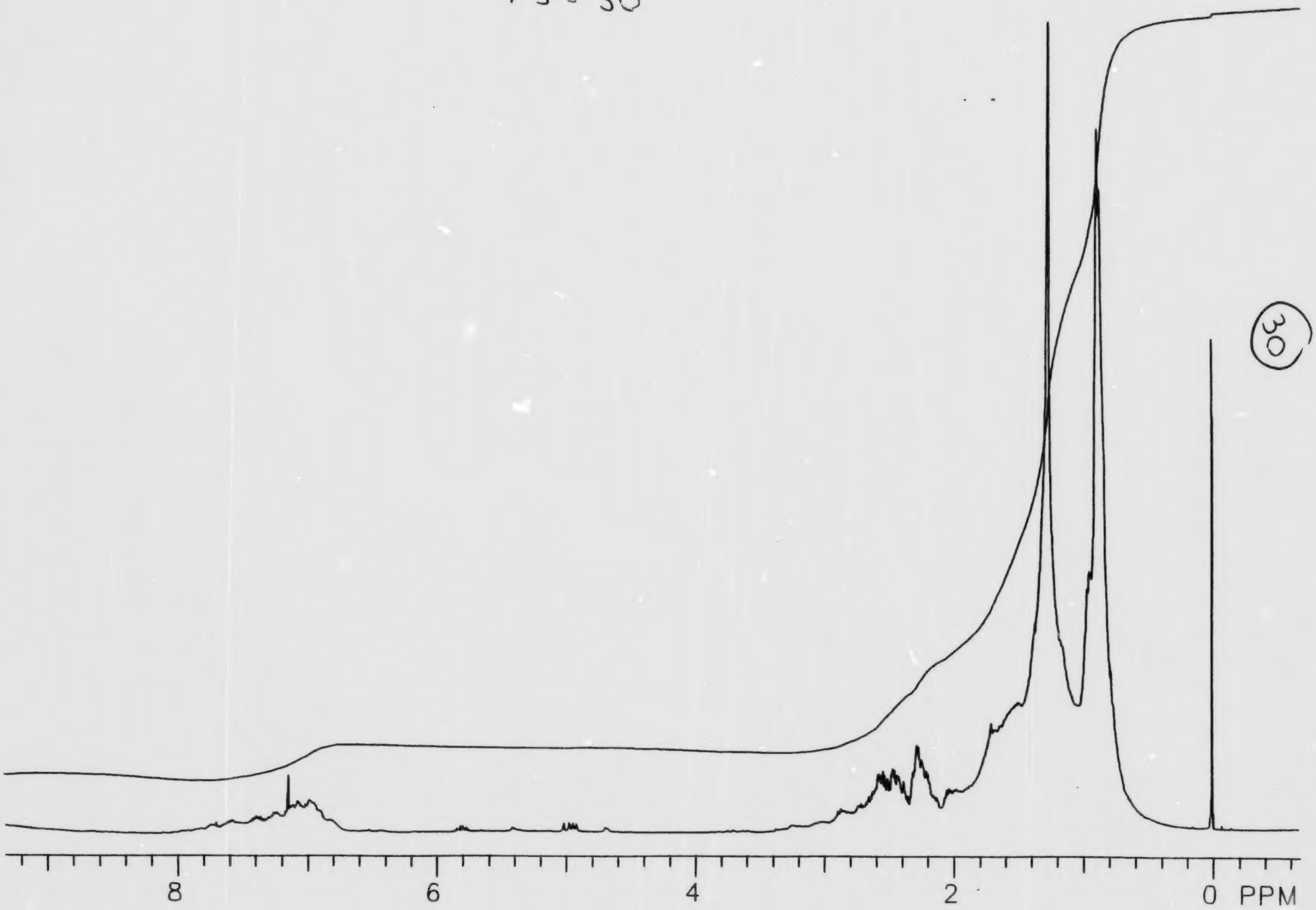
```
17  1980.19     4.952    45.556
18  1979.77     4.951    46.524
19  1972.96     4.934    47.137
20  1972.47     4.933    47.406
21  1971.59     4.931    68.432
22  1970.37     4.928    59.139
23  1969.54     4.925    54.293
24  1968.20     4.922    36.338
25  1962.73     4.908    47.808
26  1961.49     4.905    63.504
27  1960.48     4.903    56.106
28  1960.08     4.902    54.437
29  1959.29     4.900    51.558
30  1872.75     4.683    37.501
31  1872.10     4.682    38.387
32  1871.67     4.681    36.643
```

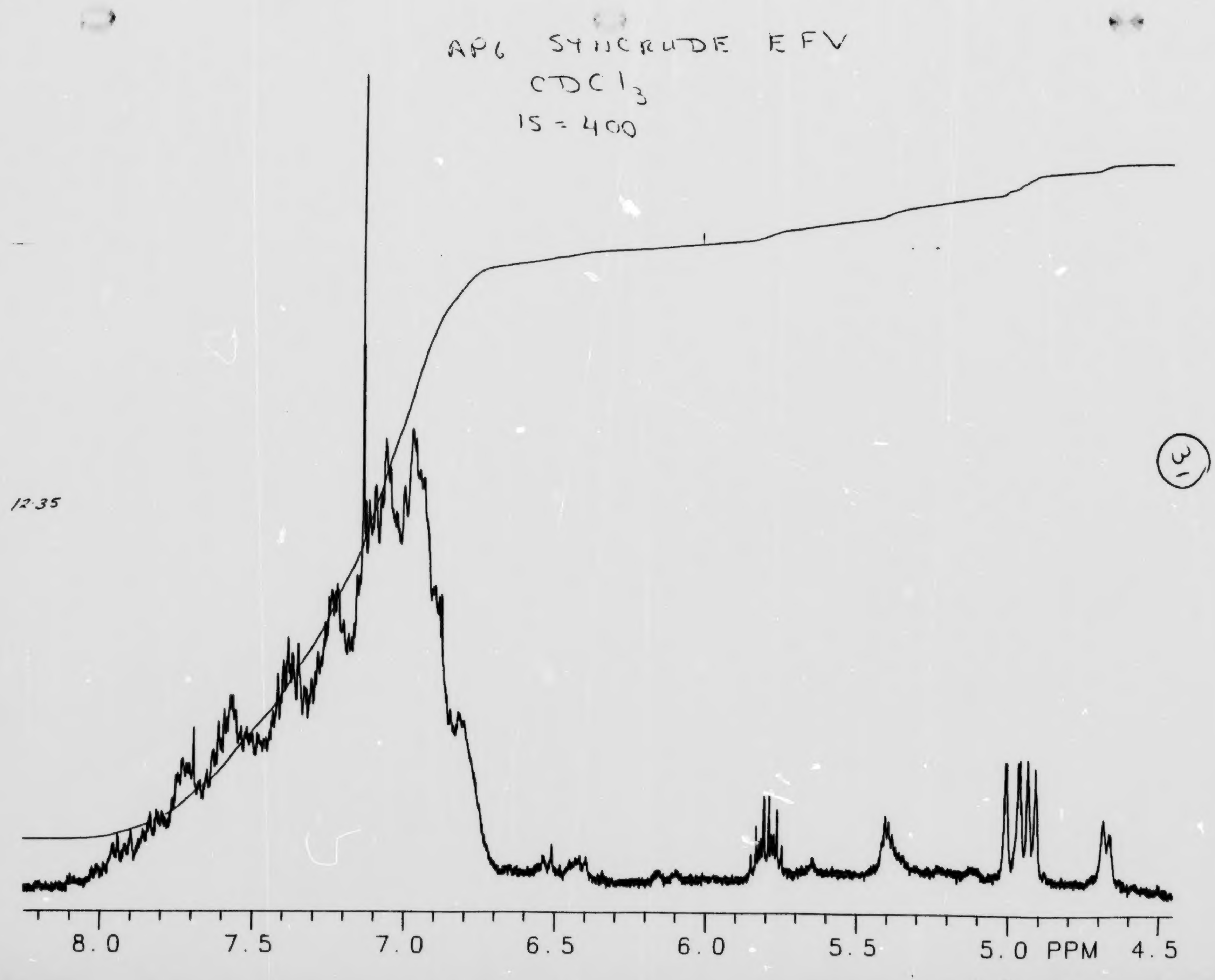
```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=    51.87
  RFL=   270.6  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01    518.96    1.298   54.968
 02    518.48    1.297   55.150
 03    518.11    1.296   55.365
 04    501.82    1.255  150.076
 05    351.48    0.879  127.365
 06    350.08    0.875  120.086
 07    347.69    0.870  115.836
 08    344.22    0.861  120.959
 09    335.36    0.839   81.085
 10    334.94    0.838   81.099
```

```
  ACQUISITION                                         PROCESSING
SFRQ   399.869          DATE  21-04-86           SE     NOT USED
TN       1.750          SOLVNT   CDCL3           LB     NOT USED
SW      4000.0          FILE     H               RE     NOT USED
AT       3.752                                   CD     NOT USED
NP       30016            DECOUPLING             CCD    NOT USED
FB        2200          DN         1.750         AF     NOT USED
BS          16          DO          74.5         FN         65536
SS           0          DM         NNN           MATH      F
PW         1.0          DLP           20
P1           0                                      SPECIAL
D1       1.000               FLAGS               TEMP   NOT USED
D2           0          IL         N             VTC         25.0
TO        -200          IN         N             PW90        13.0
NT          64          DP         Y
```

IS = 30

APL SYNCRUDE EFV
$CDCl_3$
IS = 30




APG SYNCRUDE EFV
CDCl3
IS = 400
31
12.35
8.0
7.5
7.0
6.5
6.0
5.5
5.0 PPM
4.5

IS = 4200

APC SYNCRUDE EFV
CDCl$_3$
IS = 4200

12·1

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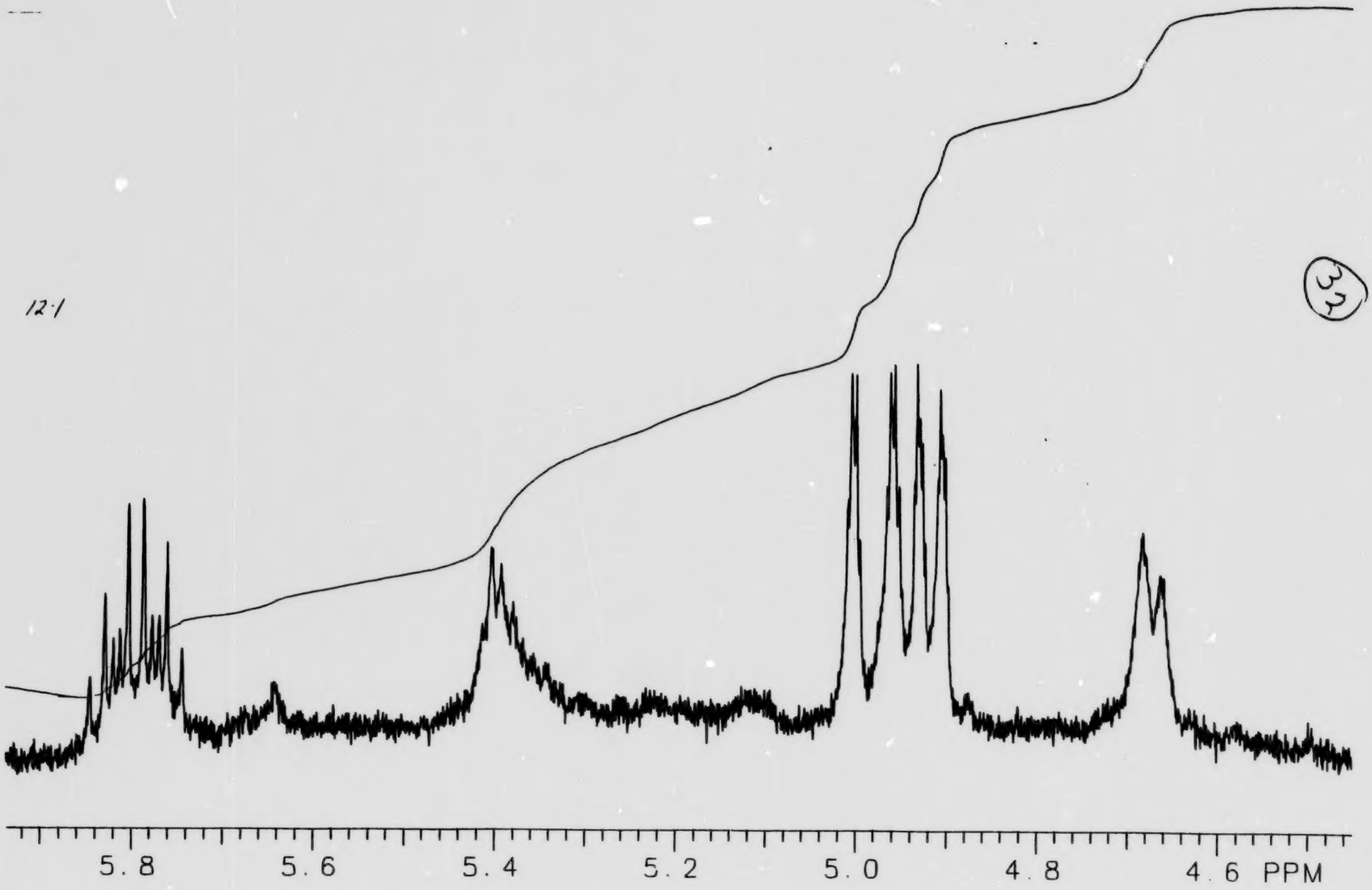
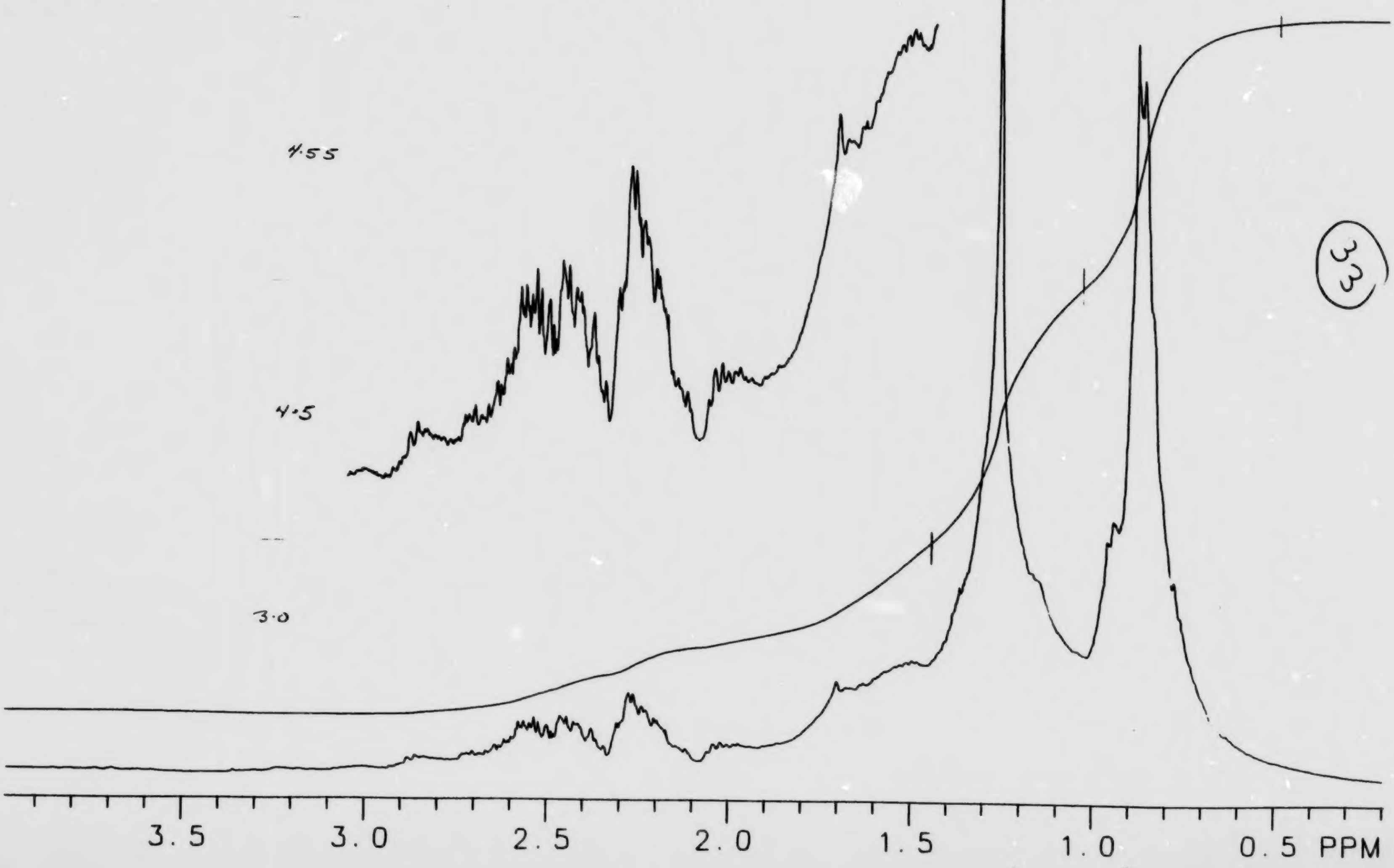


+ ⊃=30

APG SYNCRUDE EFV
$CDCl_3$
IS = 30

㉝



(34)

AF7 EDMONTON COKER 21-4-
CDCl3

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   37.34
  RFL=   261.7  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01  2331.49    5.831   38.495
 02  2321.24    5.805   58.464
 03  2314.40    5.788   59.462
 04  2304.12    5.762   46.386
 05  2161.11    5.405   51.377
 06  2157.20    5.395   41.246
 07  2002.72    5.008   40.650
 08  2001.13    5.004   74.553
 09  1999.10    4.999   76.645
 10  1997.50    4.995   41.867
 11  1985.63    4.966   42.272
 12  1984.07    4.962   72.949
 13  1982.05    4.957   77.016
 14  1980.44    4.953   49.940
 15  1973.06    4.934   45.670
 16  1971.84    4.931   73.496
 17  1970.74    4.928   63.212
 18  1969.82    4.926   61.904
 19  1962.95    4.909   43.809
 20  1961.73    4.906   70.497
 21  1960.63    4.903   60.654
 22  1959.53    4.900   59.540
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   28.32
  RFL=   261.7  RFP=        0

INDEX  FREQ      PPM   INTENSITY
01    504.44    1.262  144.962
02    359.12    0.898   32.587
03    352.43    0.881   72.538
04    350.26    0.876   34.558
05    348.49    0.872   32.432
06    345.32    0.864   38.569
07    343.67    0.859   28.756
08    341.90    0.855   29.619
```

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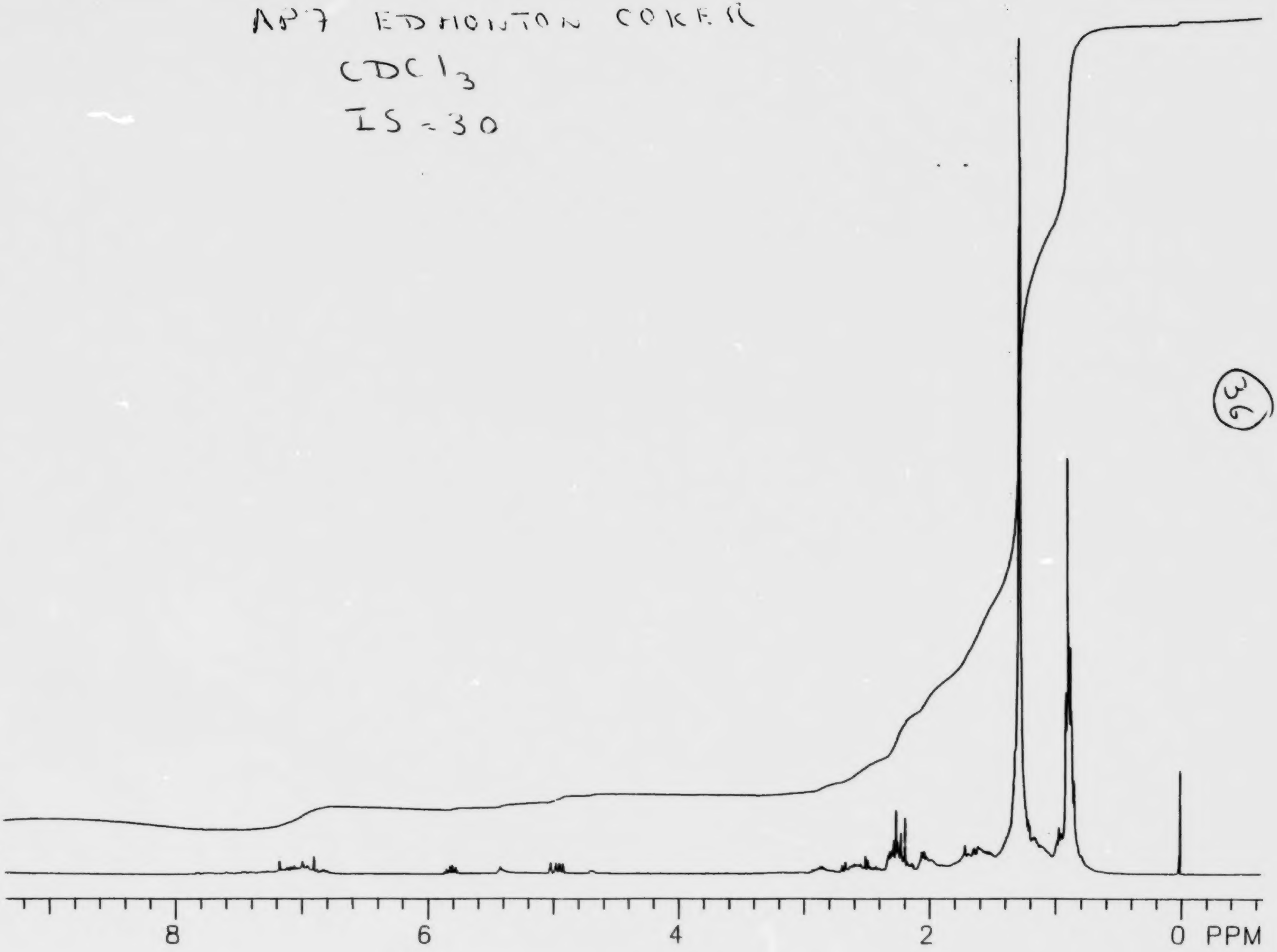
```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   20.32
 RFL=   261.7  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01   504.44    1.262  144.962
 02   359.12    0.898   32.587
 03   352.43    0.881   72.538
 04   350.26    0.876   34.558
 05   348.49    0.872   32.432
 06   345.32    0.864   30.569
 07   343.67    0.859   28.756
 08   341.90    0.855   29.619




  ACQUISITION                                         PROCESSING
SFRQ    399.869         DATE  21-04-86            SE     NOT USED
TN        1.750         SOLVNT  CDCL3             LB     NOT USED
SW       4000.0         FILE    AP7               RE     NOT USED
AT        3.752                                   CD     NOT USED
NP        30016           DECOUPLING              CCD    NOT USED
FB         2200         DN        1.750           AF     NOT USED
BS           16         DO         74.5           FN        65536
SS            0         DM          NNN           MATH      F
PW          1.0         DLP          20
P1            0                                     SPECIAL
D1        1.000              FLAGS                TEMP   NOT USED
D2            0         IL          N             VTC        25.0
TO         -200         IN          N             PW90       13.0
NT           32         DP          Y
CT           32
```

IS = 30

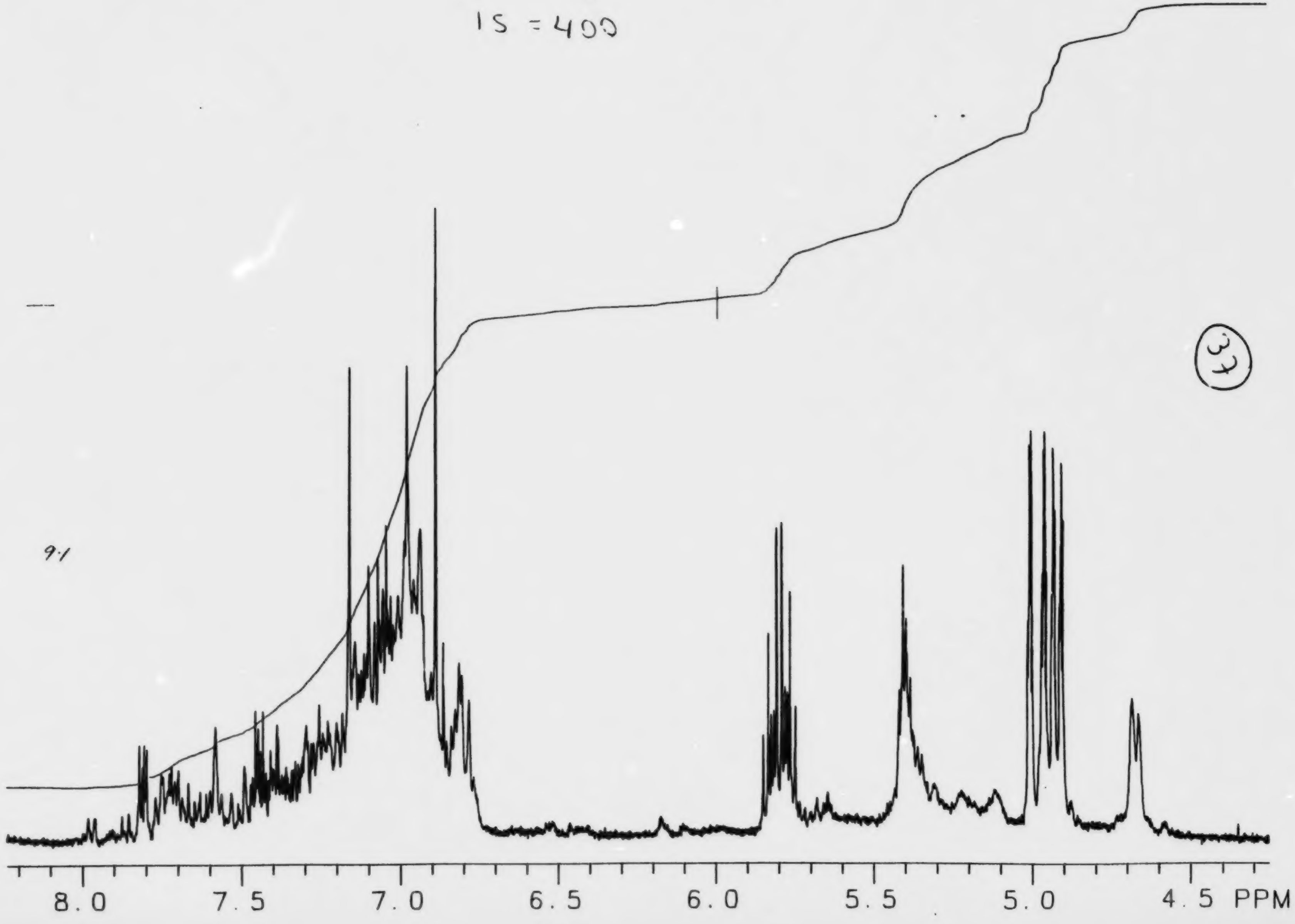


AP7 EDMONTON COKER
CDCl$_3$
IS = 30

(36)

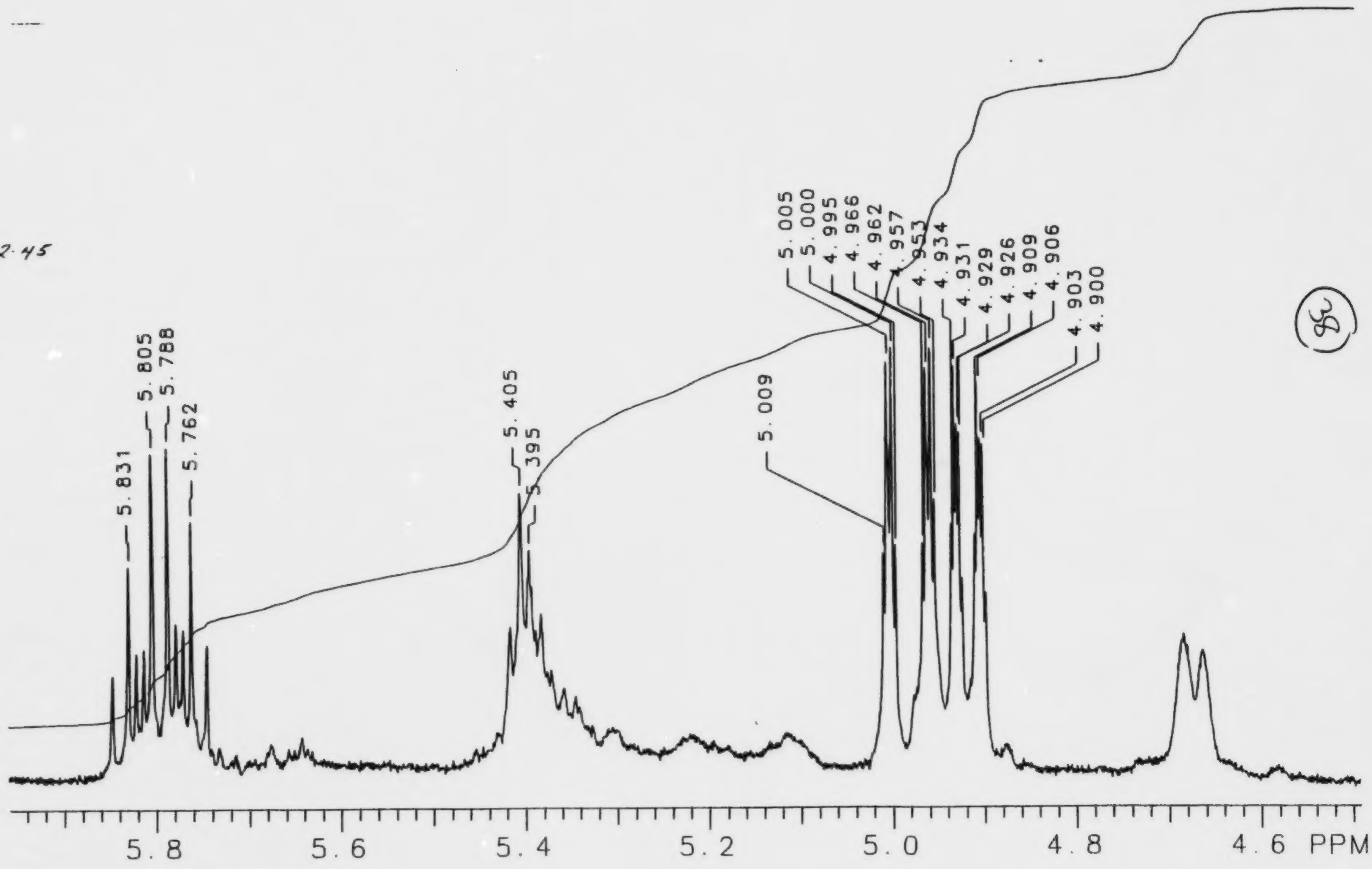
IS = 400

AP7 EDMONTON COKER
$CDCl_3$
IS = 400



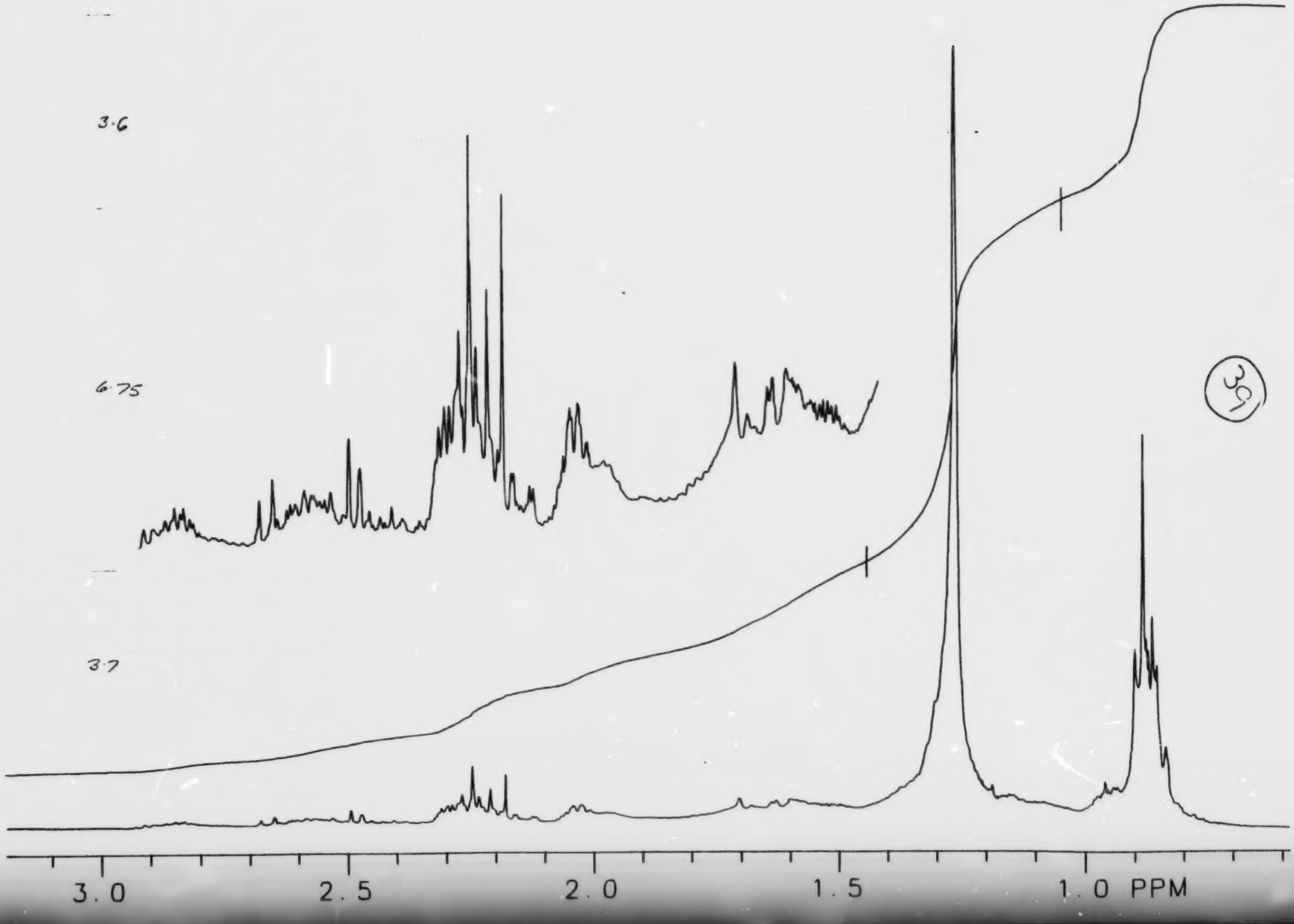
AP7 EDMONTON COKER
CDCl$_3$

12.45



(38)

AP7 EDMONTON COKER
CDCl$_3$



㊴

40

API5C 23-4-85

CDCl3

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   66.99
  RFL=   230.2  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01  2323.93    5.812   71.640
 02  2317.18    5.795   74.288
 03  2162.64    5.408  113.456
 04  2161.84    5.406  104.359
 05  2160.62    5.403   82.268
 06  2160.25    5.402   79.595
 07  2159.76    5.401   76.573
 08  2158.76    5.399   96.218
 09  2158.03    5.397   90.116
 10  2157.66    5.396   88.939
 11  2156.10    5.392   67.875
 12  2155.31    5.390   70.681
 13  2154.88    5.389   68.426
 14  2154.12    5.387   68.089
 15  2153.73    5.386   72.117
 16  2153.17    5.385   70.689
 17  2152.83    5.384   71.371
 18  2152.44    5.383   71.418
 19  2152.29    5.382   67.854
 20  2002.48    5.008  102.230
 21  2000.92    5.004   87.231
 22  2000.28    5.002  101.163
 23  1987.03    4.969   67.676
 24  1985.44    4.965  104.202
 25  1984.90    4.964   96.671
 26  1983.85    4.961   94.490
 27  1983.37    4.960  108.549
 28  1981.82    4.956   80.383
 29  1974.21    4.937   69.996
 30  1973.08    4.934   96.979
 31  1972.11    4.932   87.879
 32  1971.62    4.931   86.910
 33  1971.04    4.929   81.817
 34  1964.02    4.912   68.460
 35  1962.98    4.909   93.982
 36  1961.88    4.906   86.940
 37  1960.73    4.903   80.492
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   39.98
```

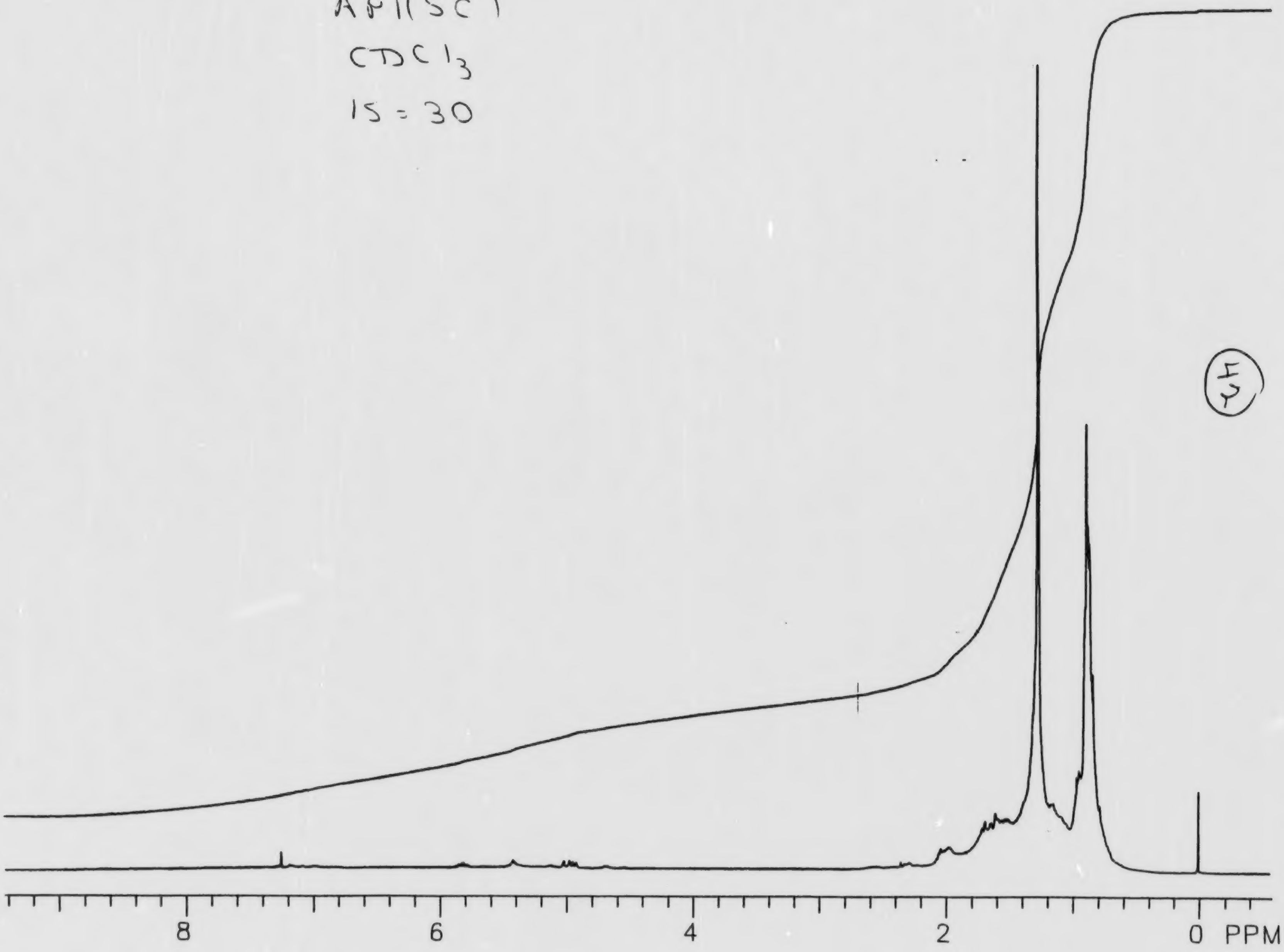
```
37  1960.73    4.903   80.492
```

41

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   39.90
 RFL=   230.2  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01   504.02    1.260  164.379
 02   358.68    0.897   47.080
 03   352.18    0.881   90.237
 04   349.89    0.875   70.794
 05   348.13    0.871   69.037
 06   345.08    0.863   70.091
 07   343.30    0.859   65.611
 08   341.54    0.854   64.882
 09   334.63    0.837   42.252
 10   333.97    0.835   42.224
```

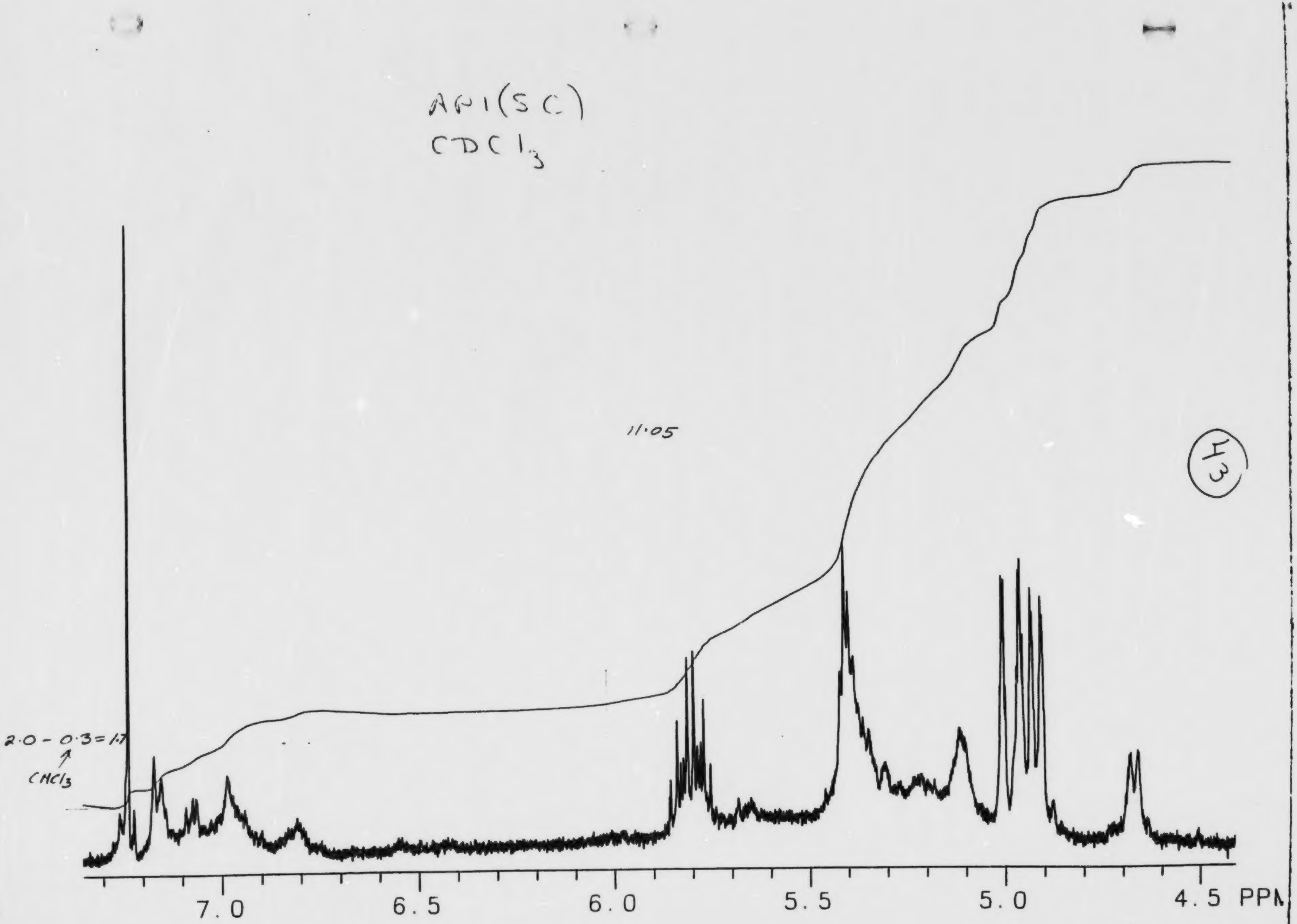
```
  ACQUISITION                                          PROCESSING
SFRQ   399.869          DATE  23-04-86          SE     NOT USED
TN       1.750          SOLVNT  CDCL3           LB     NOT USED
SW      4000.0          FILE    AP1SC           RE     NOT USED
AT       3.752                                  CD     NOT USED
NP       30016            DECOUPLING            CCD    NOT USED
FB        2200          DN       1.750          AF     NOT USED
BS          16          DO        74.5          FN        65536
SS           0          DM         NNN          MATH     F
PW         1.0          DLP          20
P1           0                                        SPECIAL
D1       1.000               FLAGS              TEMP   NOT USED
D2           0          IL         N            VTC        25.0
TO        -200          IN         N            PW90       13.0
NT          48          DP         Y
CT          48
```

IS=30



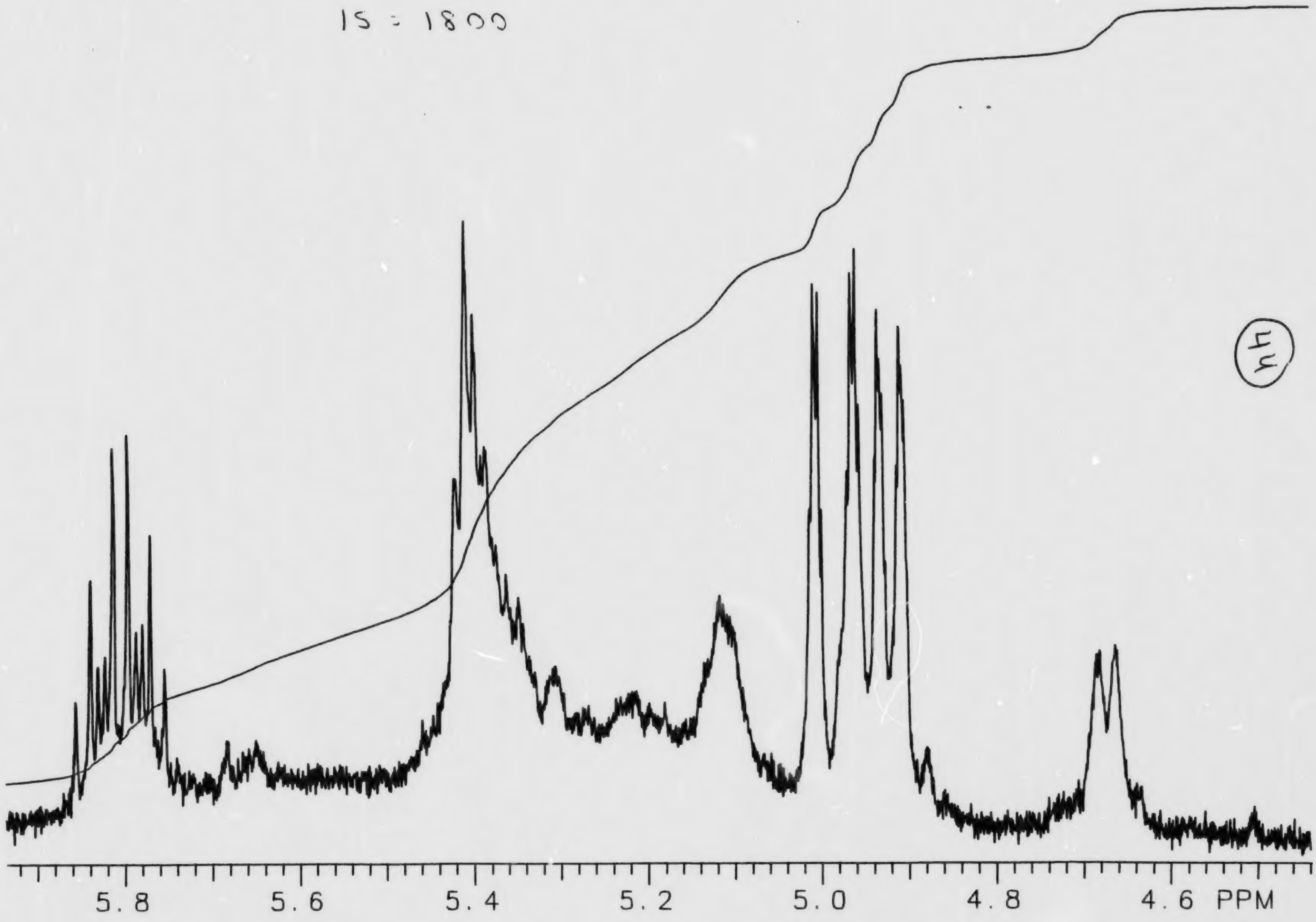
AP1(SC)
CDCl$_3$
IS = 30

㊷


AP1(SC)
CDCl3
11·05
43
2·0 - 0·3 = 1·7
CHCl3
7.0
6.5
6.0
5.5
5.0
4.5 PPM

IS = 1800

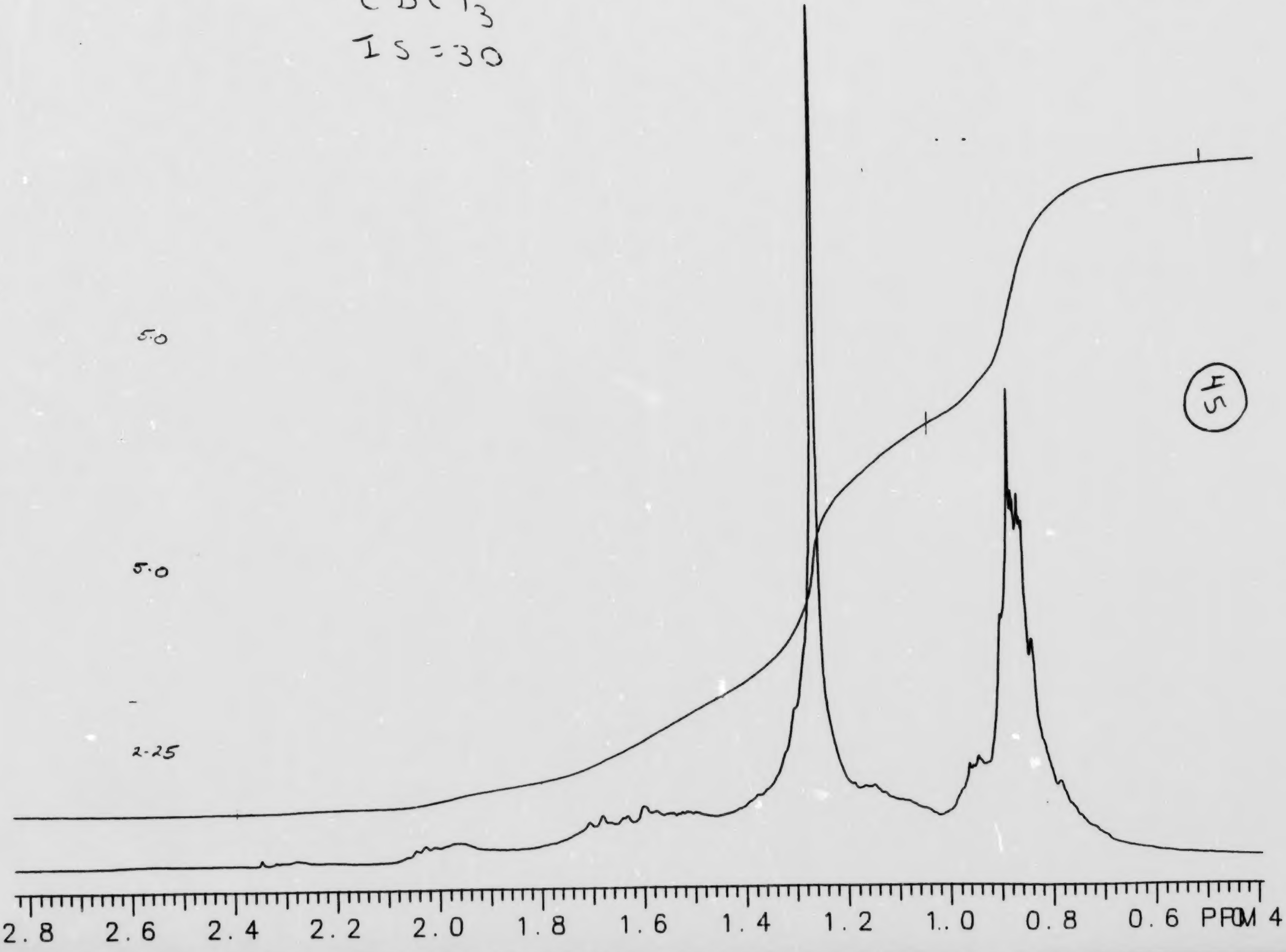
AP 1(SC)
$CDCl_3$
IS = 1800



IS=30

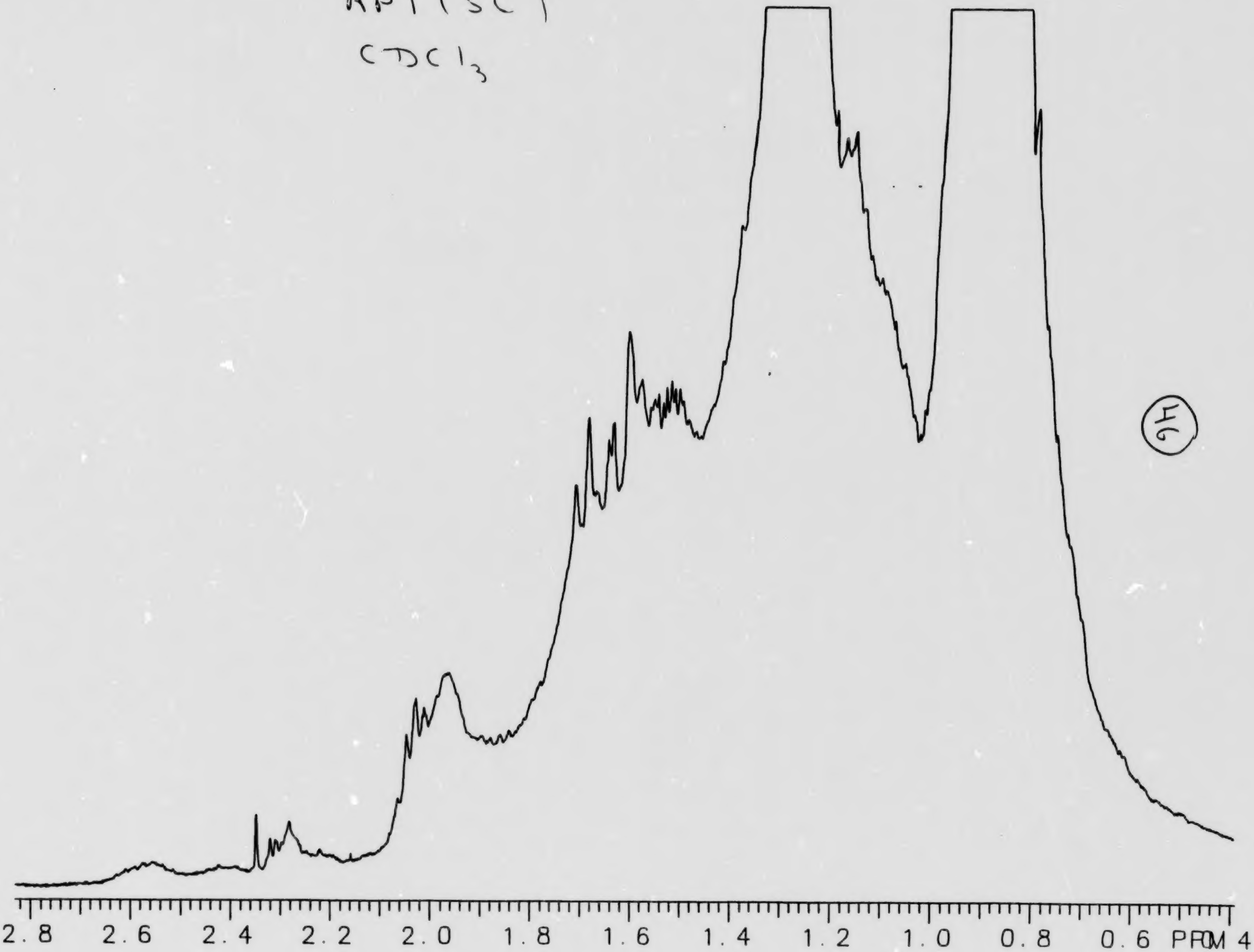
AB1(SC)
$CDCl_3$
IS=30

㊺



AP1 (SC)
$CDCl_3$

(46)



AP2 SC 23-4-86

$CDCl_3$

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   12.61
  RFL=   229.1  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01  2908.29    7.273   14.821
 02  2901.04    7.255   38.527
 03  2899.65    7.252   21.093
 04  2899.12    7.250   13.213
 05  2894.35    7.238  221.913
 06  2891.75    7.232   16.648
 07  2891.16    7.230   13.384
 08  2870.79    7.179   17.605
 09  2870.34    7.178   16.846
 10  2870.19    7.178   13.148
 11  2869.75    7.177   13.818
 12  2869.15    7.175   15.644
 13  2864.25    7.163   18.566
 14  2863.89    7.162   22.424
 15  2863.49    7.161   21.677
 16  2863.03    7.160   22.951
 17  2862.39    7.158   13.402
 18  2855.75    7.142   37.419
 19  2854.49    7.139   40.381
 20  2852.82    7.134   16.699
 21  2852.55    7.134   15.164
 22  2852.05    7.132   15.295
 23  2849.82    7.127   13.071
 24  2849.06    7.125   17.582
 25  2847.69    7.122   29.659
 26  2847.13    7.120   29.451
 27  2846.04    7.117   23.210
```

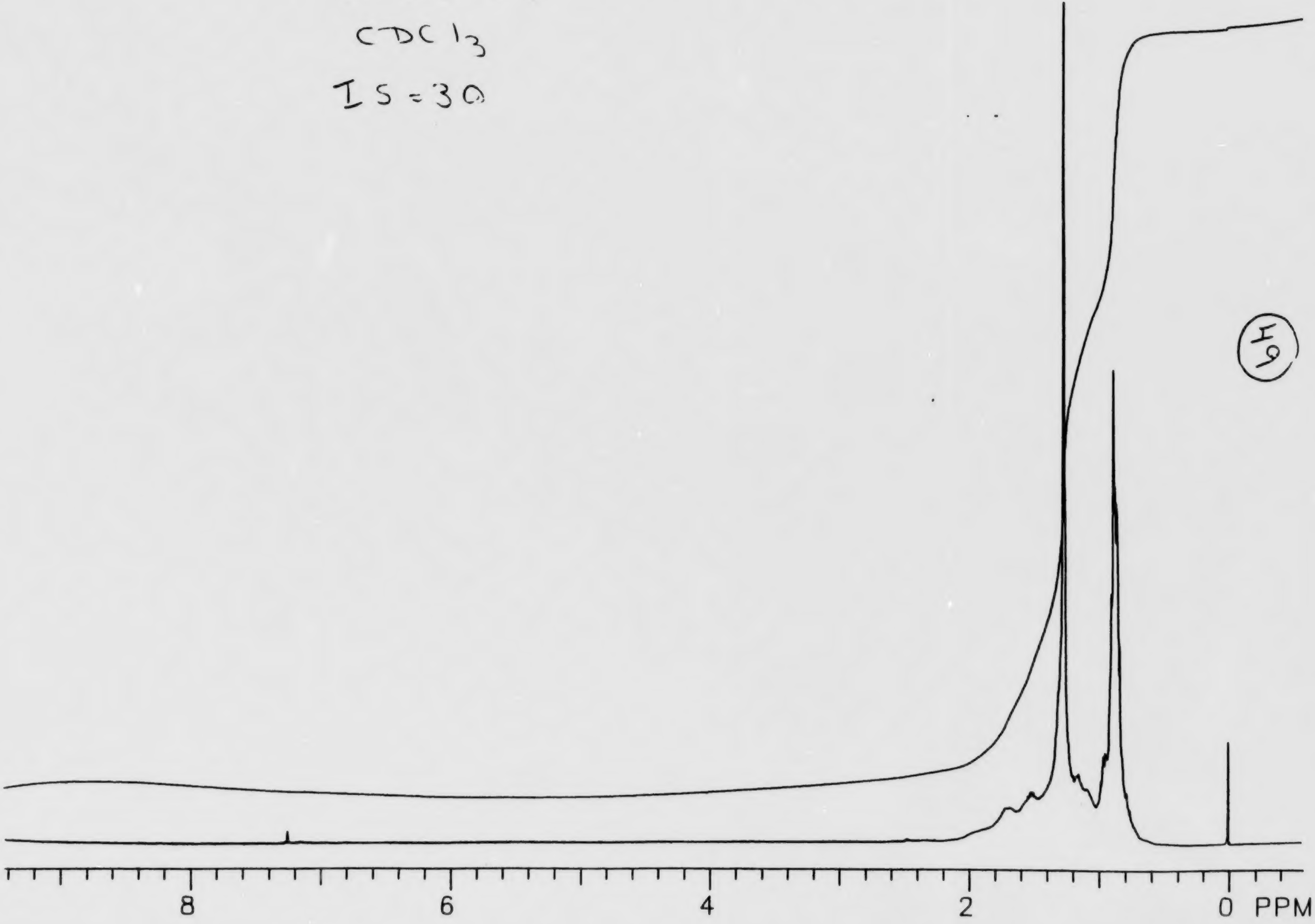
```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   37.11
  RFL=   229.1  RFP=       0

INDEX  FREQ      PPM   INTENSITY
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   37.11
 RFL=   229.1  RFP=        0

INDEX  FREQ       PPM   INTENSITY
 01   504.56     1.262  155.508
 02   359.05     0.898   42.395
 03   357.28     0.894   43.113
 04   352.43     0.881   86.060
 05   350.01     0.875   67.829
 06   348.37     0.871   66.982
 07   345.32     0.864   64.407
 08   343.30     0.859   62.897
 09   341.83     0.855   64.092
 10   334.14     0.836   39.843
```

(48)

```
                                                        PROCESSING
   ACQUISITION                                     SE      NOT USED
SFRQ    399.869          DATE  23-04-86            LB      NOT USED
TN        1.750          SOLVNT  CDCL3             RE      NOT USED
SW       4000.0          FILE    AP2SC             CD      NOT USED
AT        3.752                                    CCD     NOT USED
NP        30016             DECOUPLING             AF      NOT USED
FB         2200          DN          1.750         FN         65536
BS           16          DO           74.5         MATH      F
SS            0          DM            NNN
PW          1.0          DLP            20             SPECIAL
P1            0                                    TEMP  NOT USED
D1        1.000               FLAGS                VTC        25.0
D2            0          IL          N             PW90       13.0
TO         -200          IN          N
NT           48          DP          Y
CT           48
```

IS=30



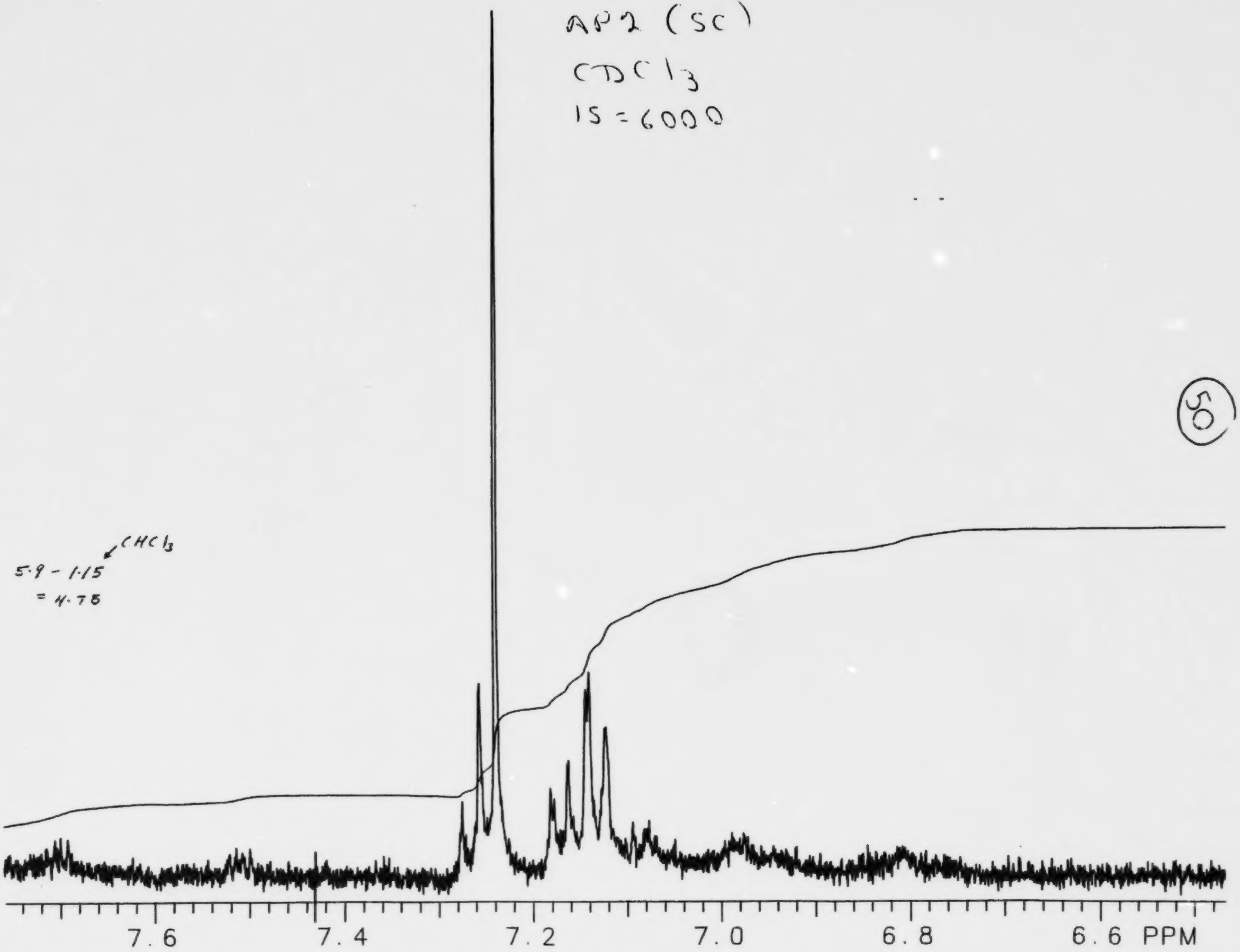
AP2(5C)
CDCl$_3$
IS=30

㊾

5 = 6000

AP2 (SC)
CDCl$_3$
IS = 6000

㊿

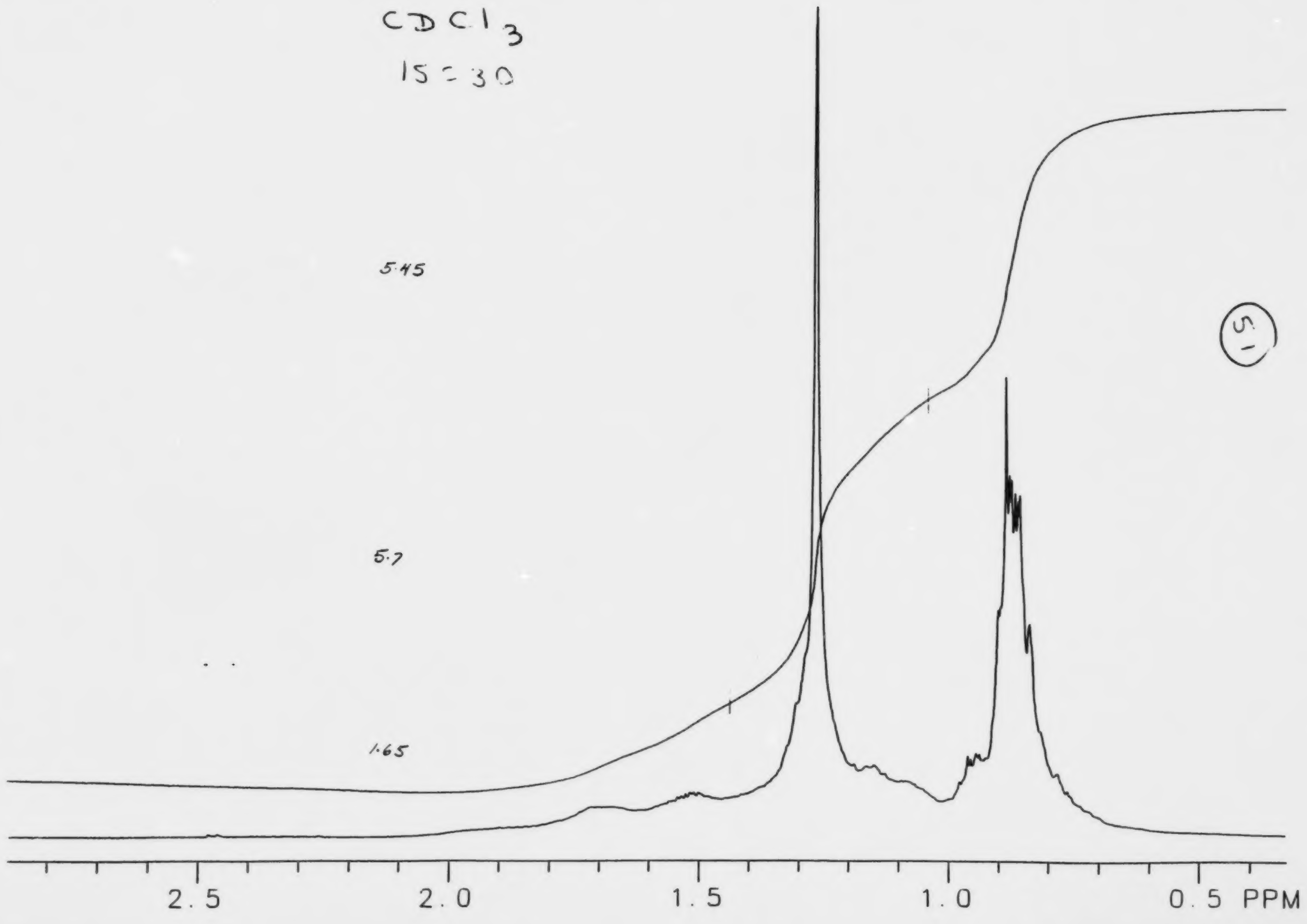


CHCl$_3$
5·9 - 1·15
= 4·75

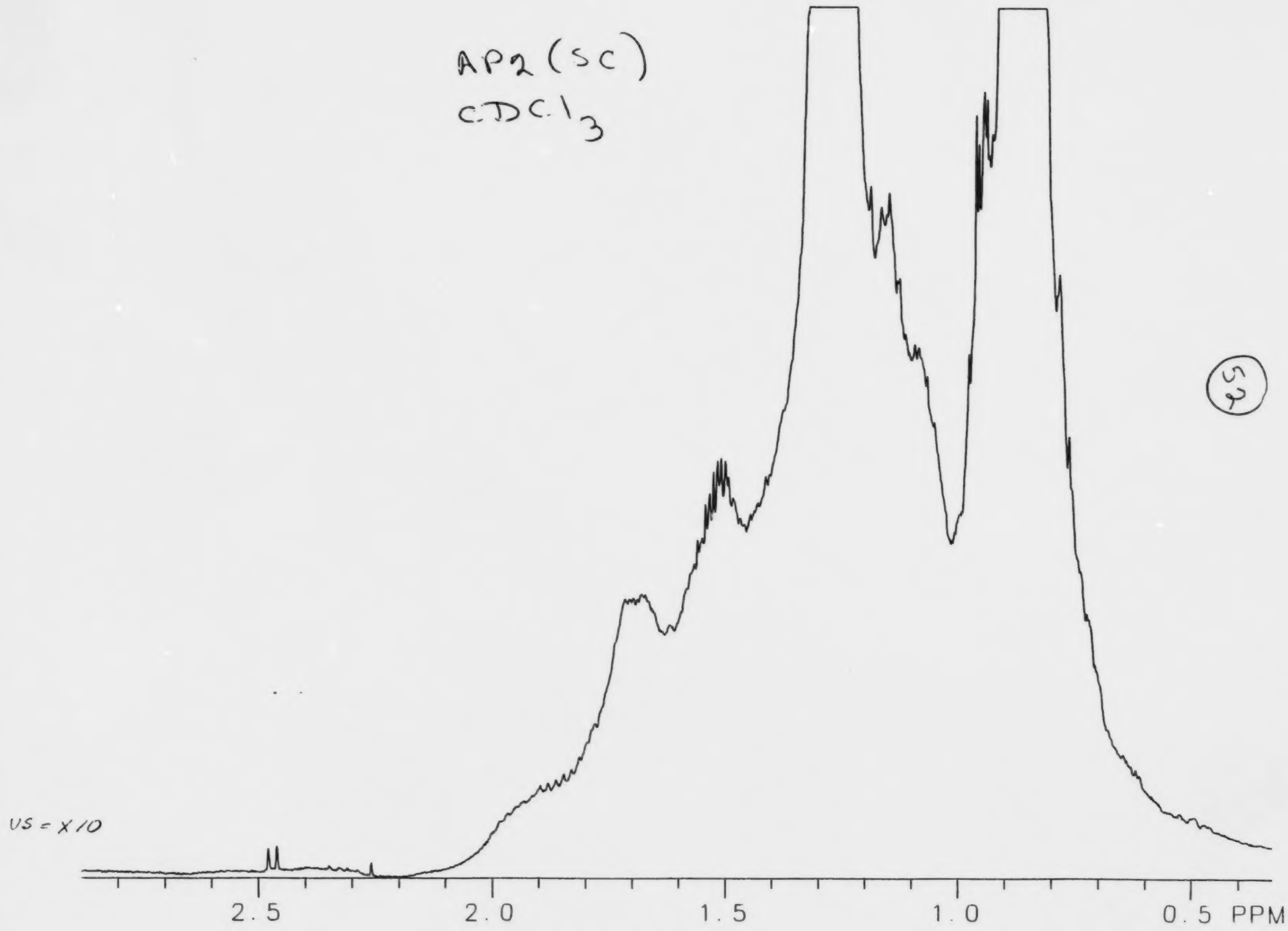
IS=30

AP2 (SC)
$CDCl_3$
IS=30

(51)



(52)



AP3SC 23-4-86
CDCl$_3$

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   38.86
 RFL=   239.9  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01  2897.70    7.247   47.611
 02  2891.47    7.231   53.858
 03  2890.38    7.228   52.813
 04  2883.54    7.211  145.838
 05  2865.35    7.166   52.062
 06  2864.00    7.163   66.029
 07  2863.64    7.161   70.124
 08  2860.58    7.154   52.729
 09  2860.07    7.153   56.317
 10  2859.74    7.152   58.129
 11  2858.51    7.149   51.605
 12  2858.15    7.148   52.728
 13  2857.48    7.146   58.337
 14  2856.87    7.145   60.739
 15  2856.32    7.143   62.097
 16  2855.59    7.141   57.631
 17  2854.80    7.139   52.281
 18  2854.12    7.138   48.675
 19  2853.75    7.137   49.855
 20  2852.66    7.134   67.330
 21  2851.07    7.130   61.100
 22  2845.79    7.117   41.201
 23  2845.09    7.115   46.630
 24  2844.42    7.113   50.243
 25  2843.84    7.112   44.989
 26  2843.01    7.110   41.253
 27  2791.62    6.981   39.912
 28  2791.13    6.980   40.719
 29  2790.55    6.979   42.033
 30  2789.91    6.977   40.461
 31  2789.37    6.976   39.633
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   38.86
 RFL=   239.9  RFP=        0

INDEX  FREQ      PPM   INTENSITY
```

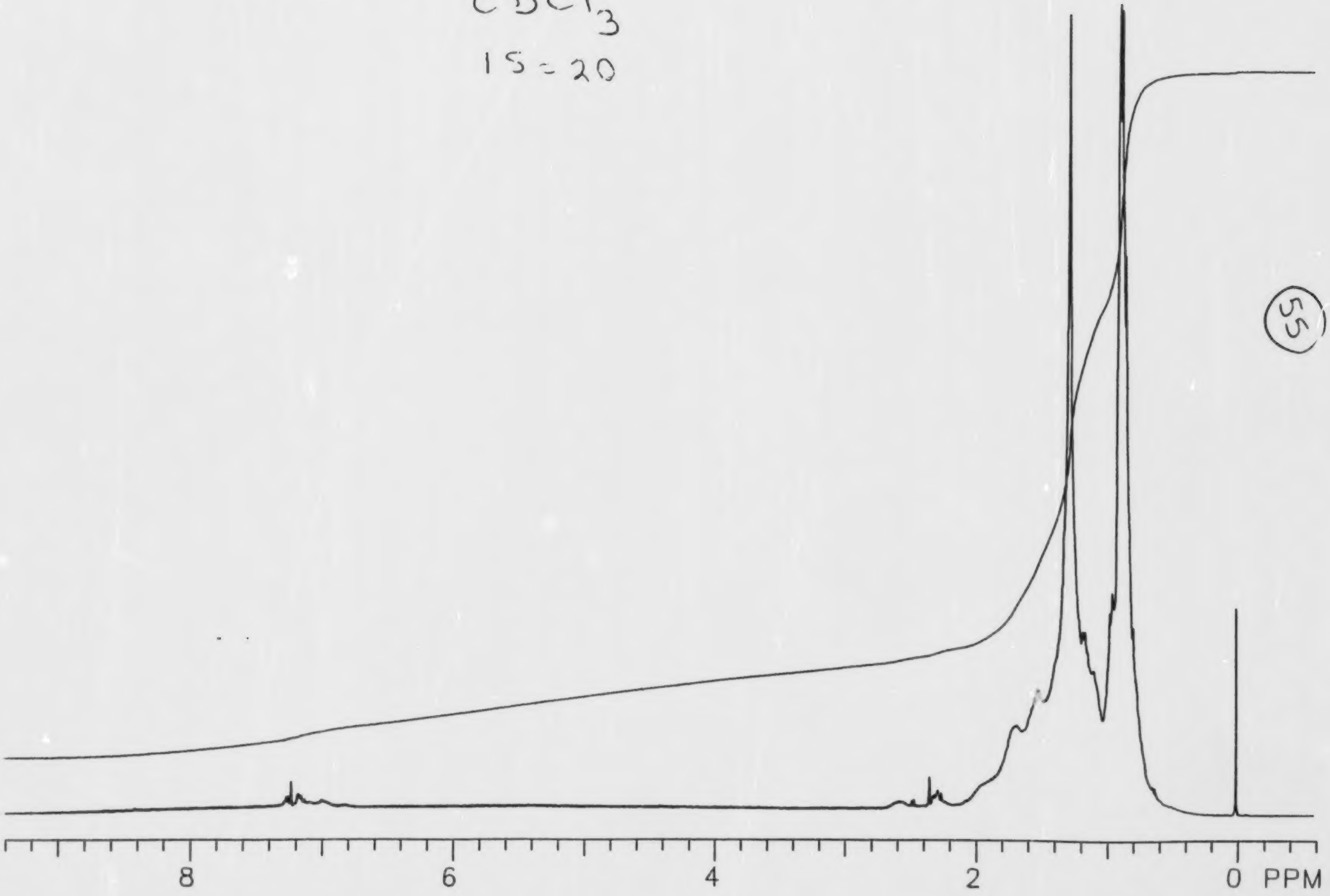
```
31  2789.37     6.976   39.633
```

54

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   30.86
 RFL=   239.9  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01   504.93    1.263  123.599
 02   363.14    0.908   51.044
 03   356.61    0.892   81.193
 04   352.28    0.881  114.564
 05   350.08    0.875  125.497
 06   348.37    0.871  114.476
 07   346.60    0.867  106.980
 08   343.37    0.859  122.924
 09   342.39    0.856  117.921
 10   341.78    0.855  118.109
 11   335.19    0.838   83.610
 12   326.70    0.817   43.171
 13   325.48    0.814   42.050
```

```
  ACQUISITION                                      PROCESSING
SFRQ   399.869        DATE  23-04-86          SE     NOT USED
TN       1.750        SOLVNT  CDCL3           LB     NOT USED
SW      4000.0        FILE    AP3SC           RE     NOT USED
AT       3.752                                CD     NOT USED
NP       30016          DECOUPLING            CCD    NOT USED
FB        2200        DN        1.750         AF     NOT USED
BS          16        DO         74.5         FN        65536
SS           0        DM          NNN         MATH      F
PW         1.0        DLP          20
P1           0                                  SPECIAL
D1       1.000            FLAGS               TEMP   NOT USED
D2           0        IL         N            VTC        25.0
TO        -200        IN         N            PW90       13.0
NT          48        DP         Y
CT          48
```

AP3 (SC)
$CDCl_3$
IS = 20



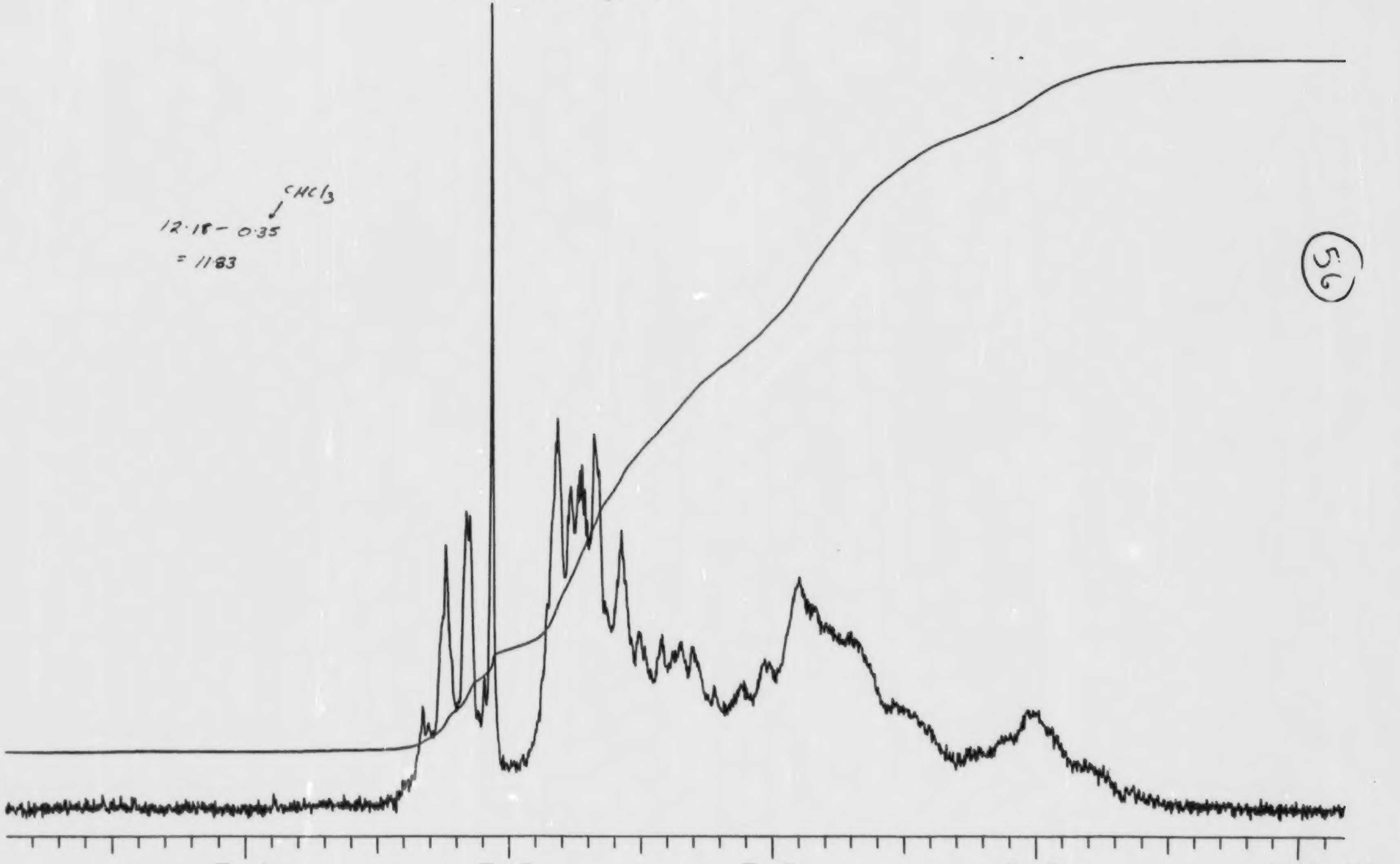
(55)

IS = 2200

AP·3 (SC)
$CDCl_3$
IS = 2200

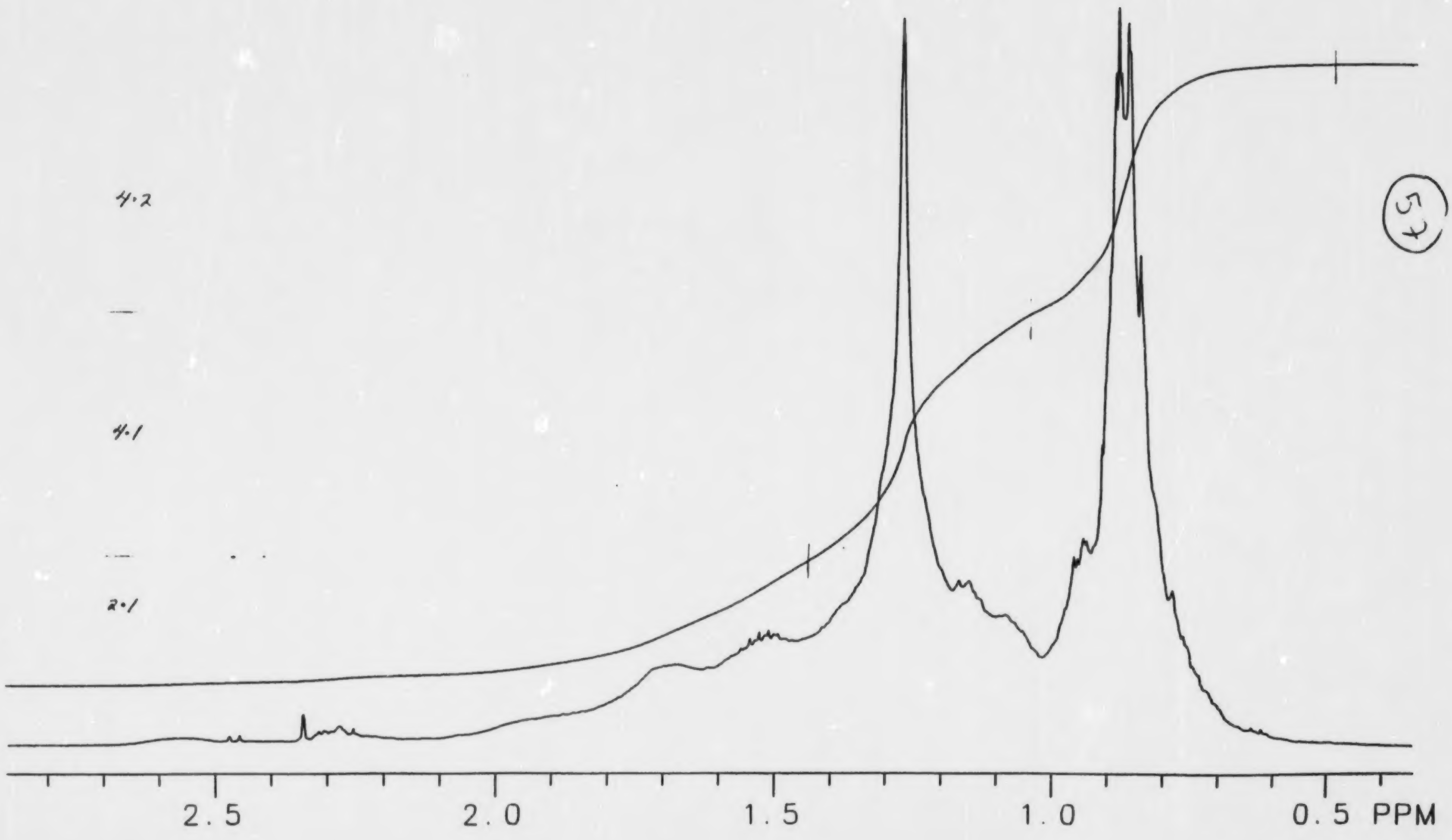
$CHCl_3$
12·18 − 0·35
= 11·83

(56)



IS=20

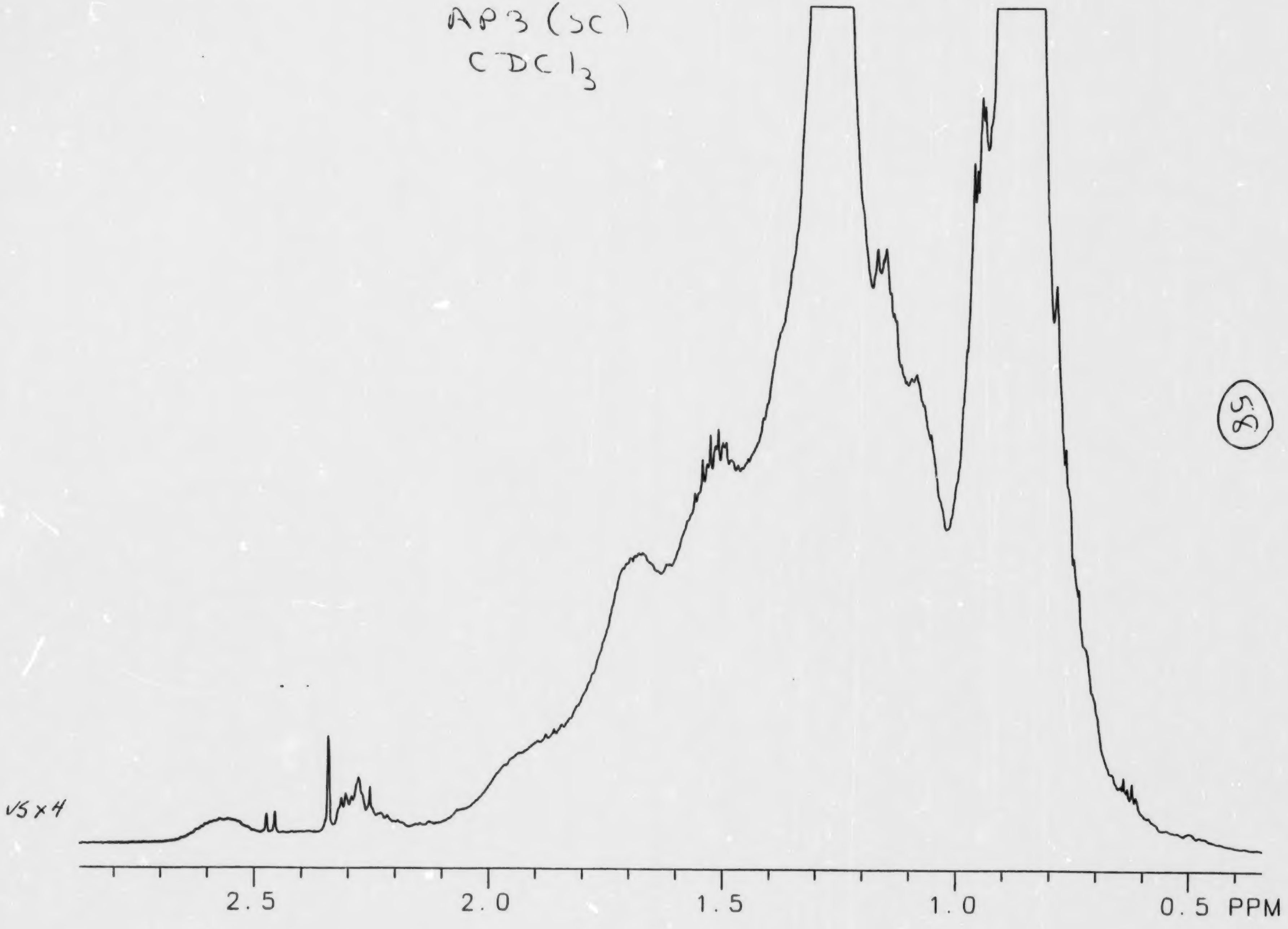
AP3 (SC)
$CDCl_3$
IS = 20



(57)

(58)

AP3 (SC)
$CDCl_3$



(59)

AP4SC 23-4-86

$CDCl_3$

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   16.50
  RFL=   239.8  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01  2899.02    7.250   42.191
 02  2897.40    7.246   21.093
 03  2891.60    7.231   97.562
 04  2886.32    7.218   30.881
 05  2884.37    7.213  103.452
 06  2864.23    7.163  112.571
 07  2863.59    7.161  124.042
 08  2860.81    7.154   58.088
 09  2860.17    7.153   57.325
 10  2859.25    7.150   49.074
 11  2858.80    7.150   51.025
 12  2857.61    7.146   64.791
 13  2857.00    7.145   77.901
 14  2856.44    7.143   82.692
 15  2855.67    7.141   72.538
 16  2855.12    7.140   54.773
 17  2854.21    7.138   41.430
 18  2853.82    7.137   37.257
 19  2852.41    7.133   51.632
 20  2845.36    7.116   17.799
 21  2844.69    7.114   16.597
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   49.65
  RFL=   239.8  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01   936.43    2.342   76.106
 02   935.97    2.341   76.332
 03   514.69    1.287   52.574
 04   505.17    1.263  136.379
 05   362.41    0.906   50.914
 06   358.75    0.897   76.215
 07   355.21    0.888   99.973
 08   352.58    0.882  132.955
 09   350.57    0.877  107.178
 10   347.88    0.870  153.005
```

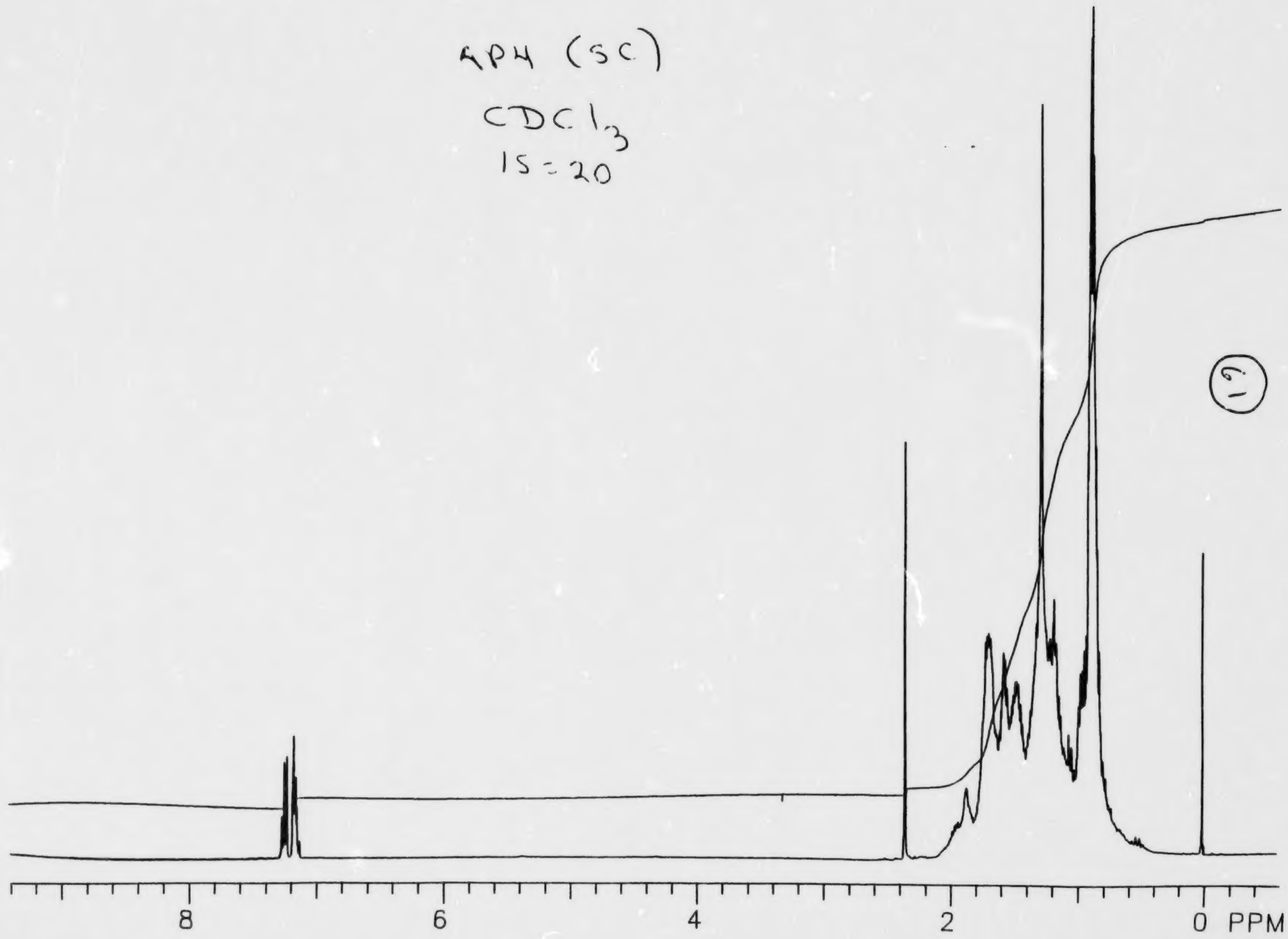
60

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   49.65
  RFL=   239.8  RFP=       0

INDEX  FREQ       PPM   INTENSITY
 01   936.43     2.342   76.106
 02   935.97     2.341   76.332
 03   514.69     1.287   52.574
 04   505.17     1.263  136.379
 05   362.41     0.906   50.914
 06   358.75     0.897   76.215
 07   355.21     0.888   99.973
 08   352.58     0.882  132.855
 09   350.57     0.877  107.178
 10   347.88     0.870  153.005
 11   346.35     0.866  110.657
 12   345.25     0.863  112.344
 13   343.42     0.859  102.803
 14   341.56     0.854  123.646
 15   335.24     0.838   69.775
 16   332.38     0.831   51.458
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   49.65
  RFL=   239.8  RFP=       0

INDEX  FREQ       PPM   INTENSITY
 01   936.43     2.342   77.359
 02   935.97     2.341   77.588
```

```
                                                          PROCESSING
  ACQUISITION                                        SE    NOT USED
SFRQ   399.869         DATE  23-04-86                LB    NOT USED
TN       1.750         SOLVNT  CDCL3                 RE    NOT USED
SW      4000.0         FILE    AP4SC                 CD    NOT USED
AT       3.752                                       CCD   NOT USED
NP       30016            DECOUPLING                 AF    NOT USED
FB        2200         DN        1.750               FN       65536
BS          16         DO         74.5               MATH     F
SS           0         DM         NNN
PW         1.0         DLP          20                 SPECIAL
P1           0                                       TEMP  NOT USED
D1       1.000               FLAGS                   VTC       25.0
D2           0         IL         N                  PW90      13.0
TO        -200         IN         N
NT          40         DP         Y
```

IS=20

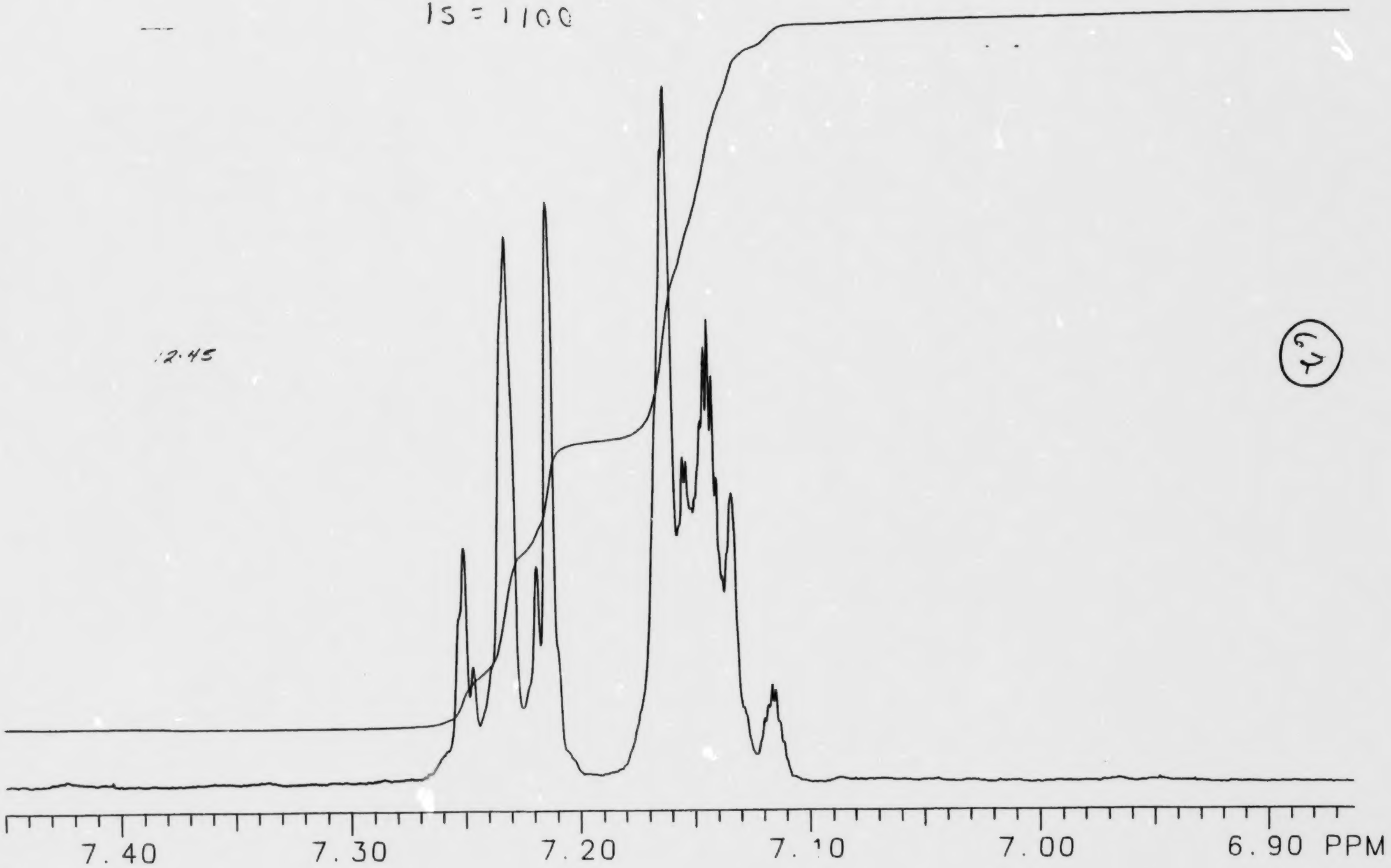

(61)

IS= 1100

AP4 (SC)

$CDCl_3$

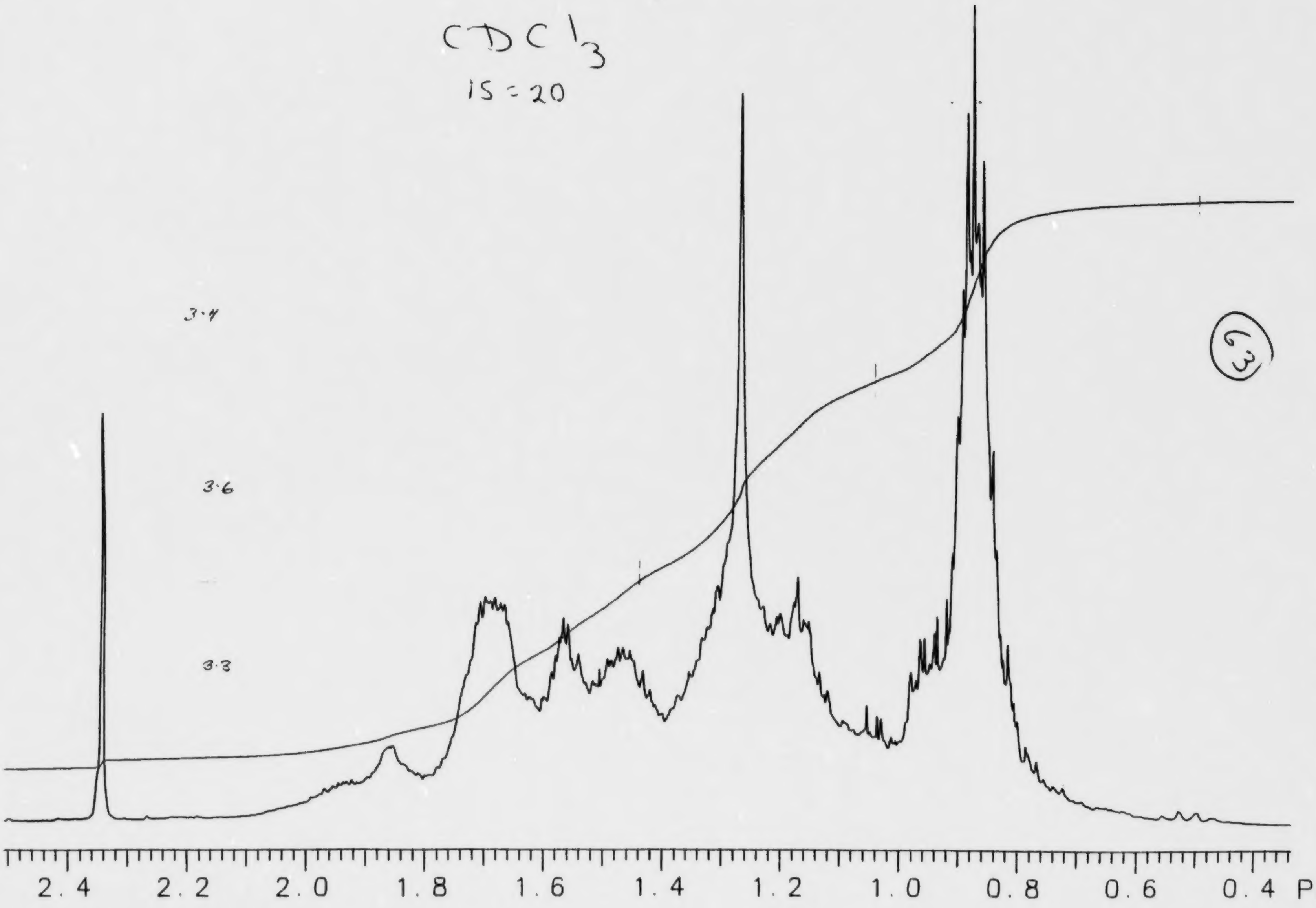
IS = 1100



IS=20

AP4 (SC)
$CDCl_3$
IS=20

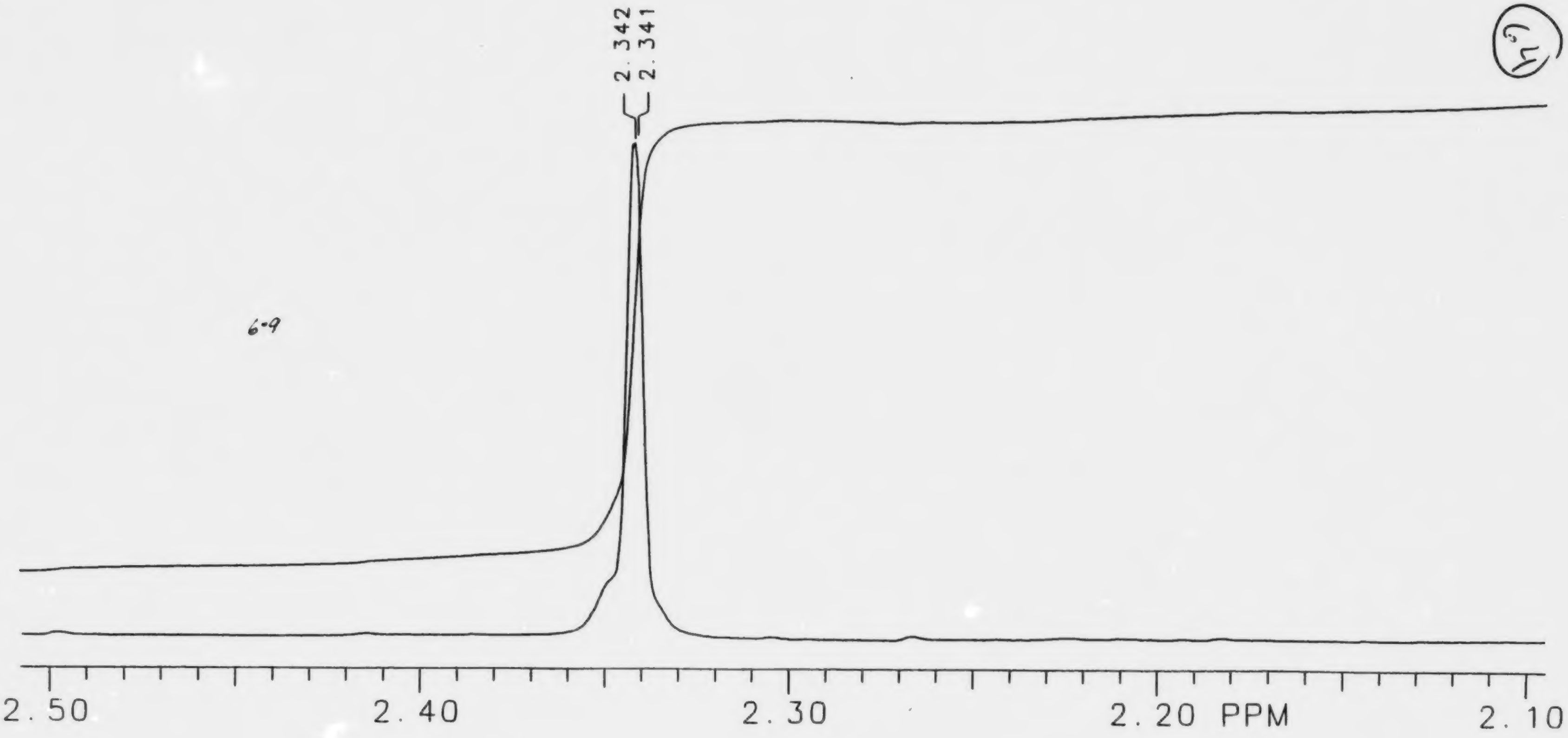
(63)



IS = 1000

AP4 (SC)
$CDCl_3$
IS = 1000

(6.4)



APS SC 23-4-86 65

$CDCl_3$

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   12.61
  RFL=   230.6  RFP=       0

INDEX  FREQ       PPM   INTENSITY
 01   2903.04    7.260   29.770
 02   2901.58    7.256   15.604
 03   2895.57    7.241   73.616
 04   2892.51    7.234   53.617
 05   2890.32    7.228   20.128
 06   2888.25    7.223   75.020
 07   2867.52    7.171   94.129
 08   2865.60    7.166   41.895
 09   2864.84    7.164   49.054
 10   2864.20    7.163   47.757
 11   2863.28    7.161   41.262
 12   2862.79    7.159   40.221
 13   2861.57    7.156   50.516
 14   2860.88    7.155   60.300
 15   2860.35    7.153   65.329
 16   2859.56    7.151   60.814
 17   2858.76    7.149   49.132
 18   2856.44    7.143   44.296
 19   2853.63    7.136   15.660
 20   2850.21    7.128   13.908
 21   2849.33    7.126   16.929
 22   2848.67    7.124   16.458
 23   2847.94    7.122   12.797
```

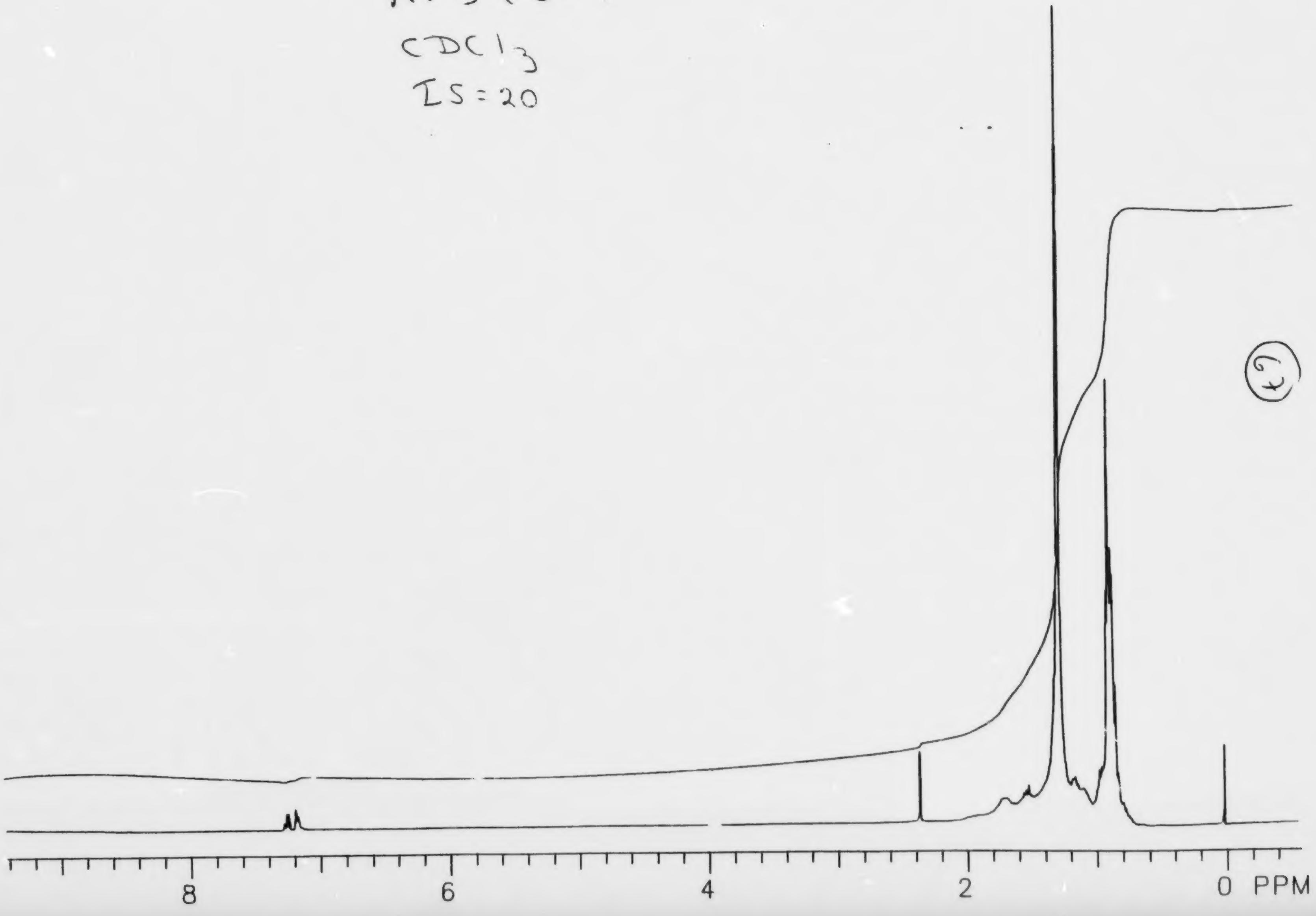
66

AP5SC
CDCl3

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   12.61
  RFL=   230.6  RFP=       0

INDEX  FREQ       PPM   INTENSITY
 01    938.05    2.348   13.792
 02    527.88    1.320   16.503
 03    527.51    1.319   16.523
 04    520.92    1.303   26.073
 05    504.68    1.262  161.849
 06    359.29    0.899   41.229
 07    357.46    0.894   37.723
 08    352.55    0.882   86.659
 09    350.26    0.876   61.408
 10    348.67    0.872   54.411
 11    345.62    0.864   55.182
 12    343.54    0.859   52.287
 13    341.96    0.855   51.437
 14    335.00    0.838   29.331
 15    333.97    0.835   28.544
```

```
                                                   PROCESSING
   ACQUISITION                                  SE     NOT USED
SFRQ   399.869       DATE  23-04-86             LB     NOT USED
TN       1.750       SOLVNT  CDCL3              RE     NOT USED
SW      4000.0       FILE    AP5SC              CD     NOT USED
AT       3.752                                  CCD    NOT USED
NP       30016          DECOUPLING              AF     NOT USED
FB        2200       DN          1.750          FN        65536
BS          16       DO           74.5          MATH      F
SS           0       DM          NNN
PW         1.0       DLP            20              SPECIAL
P1           0                                  TEMP  NOT USED
D1       1.000             FLAGS                VTC        25.0
D2           0       IL          N              PW90       13.0
TO        -200       IN          N
NT          48       DP          Y
CT          48
```

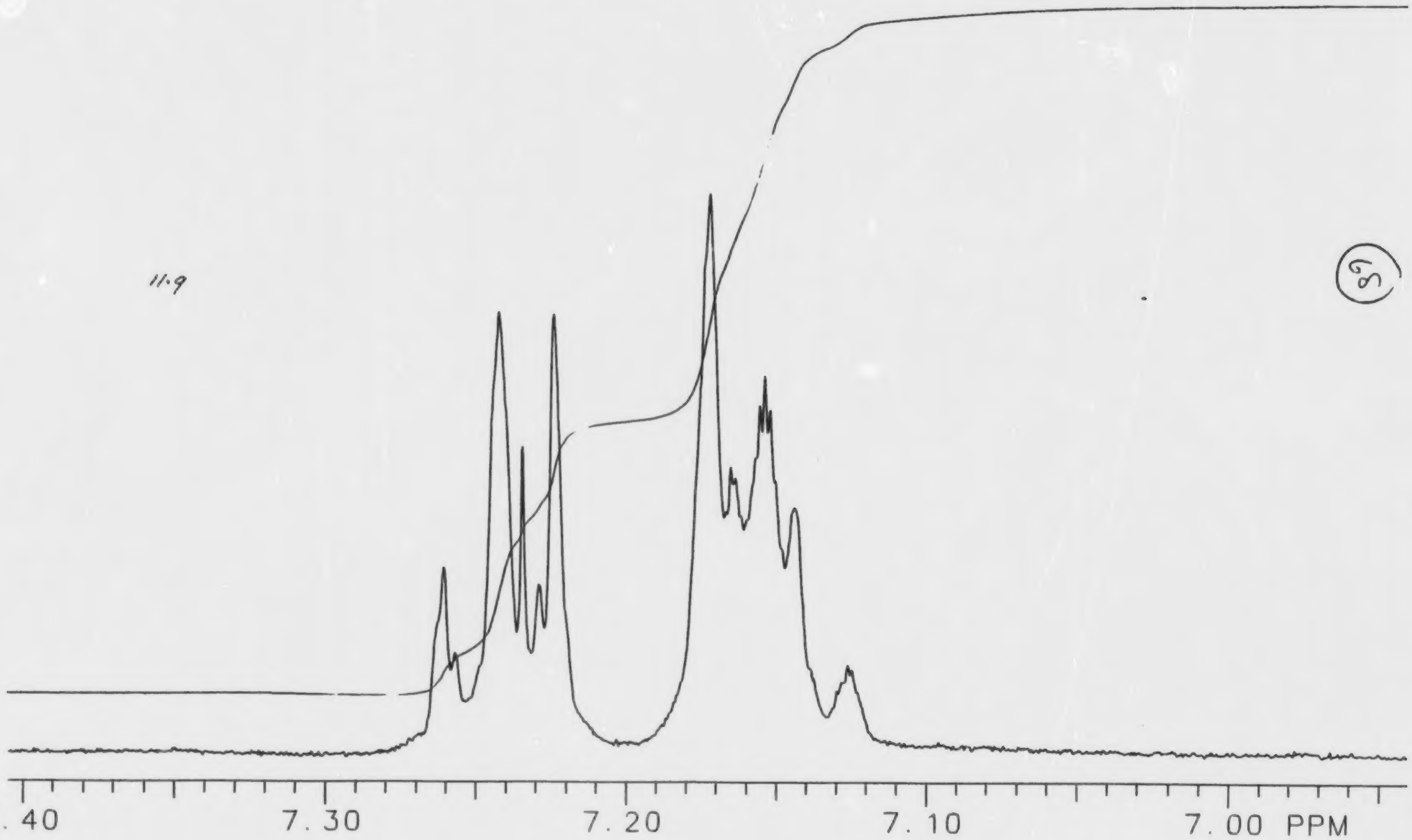
APS (SC)
CDCl$_3$
IS=20



(67)

IS = 2000

AP 5 (SC)
$CDCl_3$
IS = 2000

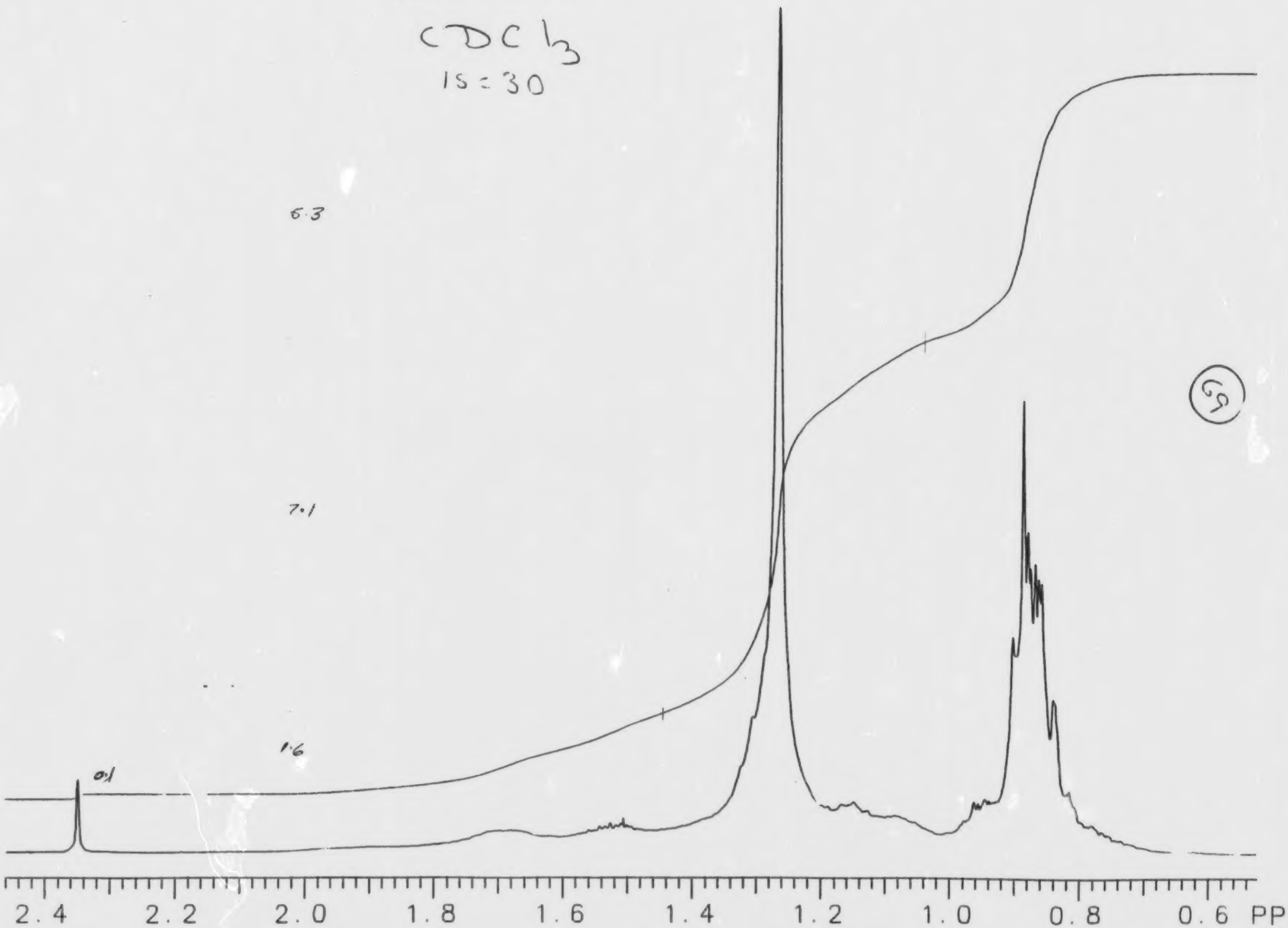


11.9

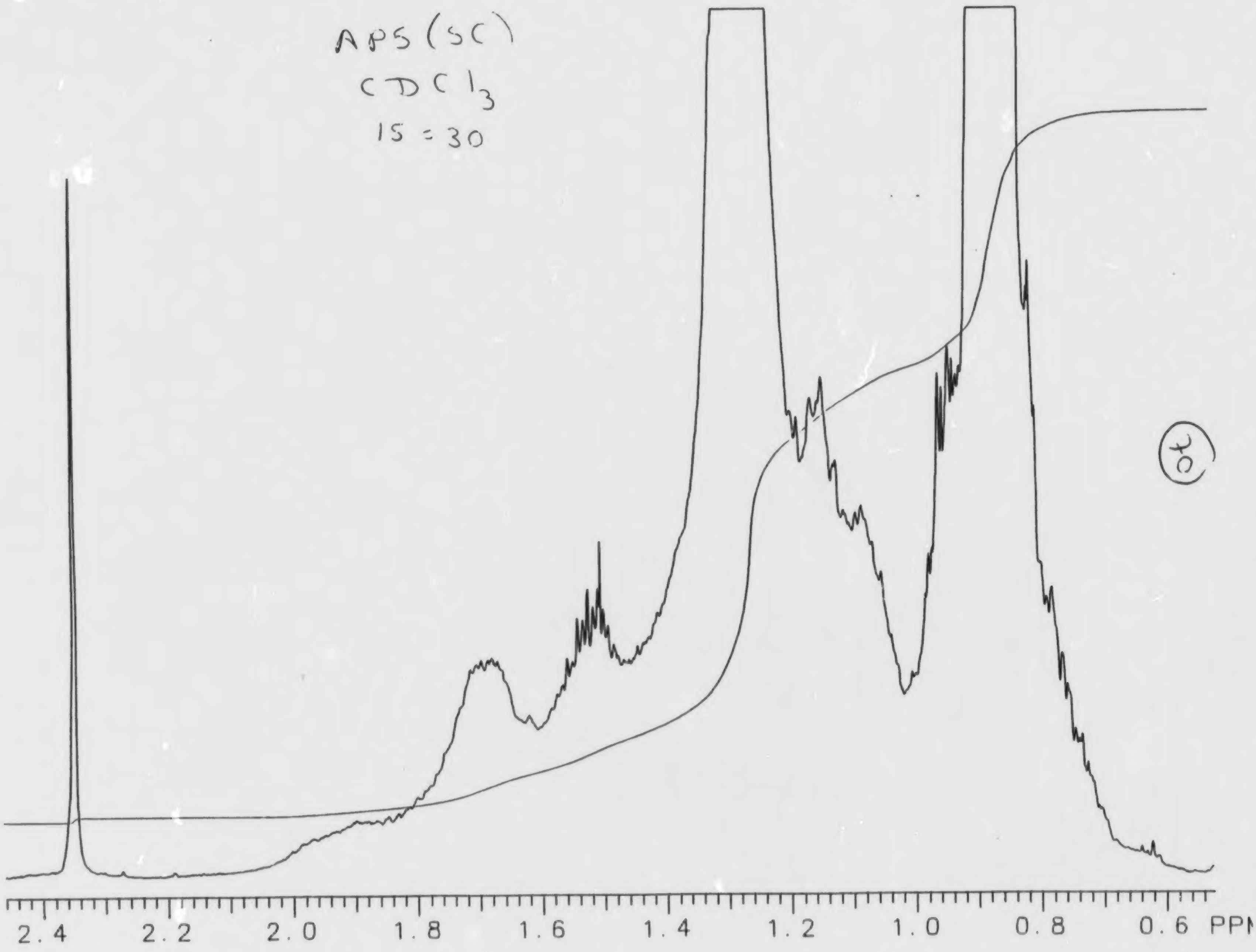
(68)

5-30

AP5 (SC)
CDCl3
IS = 30



(69)



APS (SC)
$CDCl_3$
IS = 30

⑩

(71)

AF65C 23-4-86

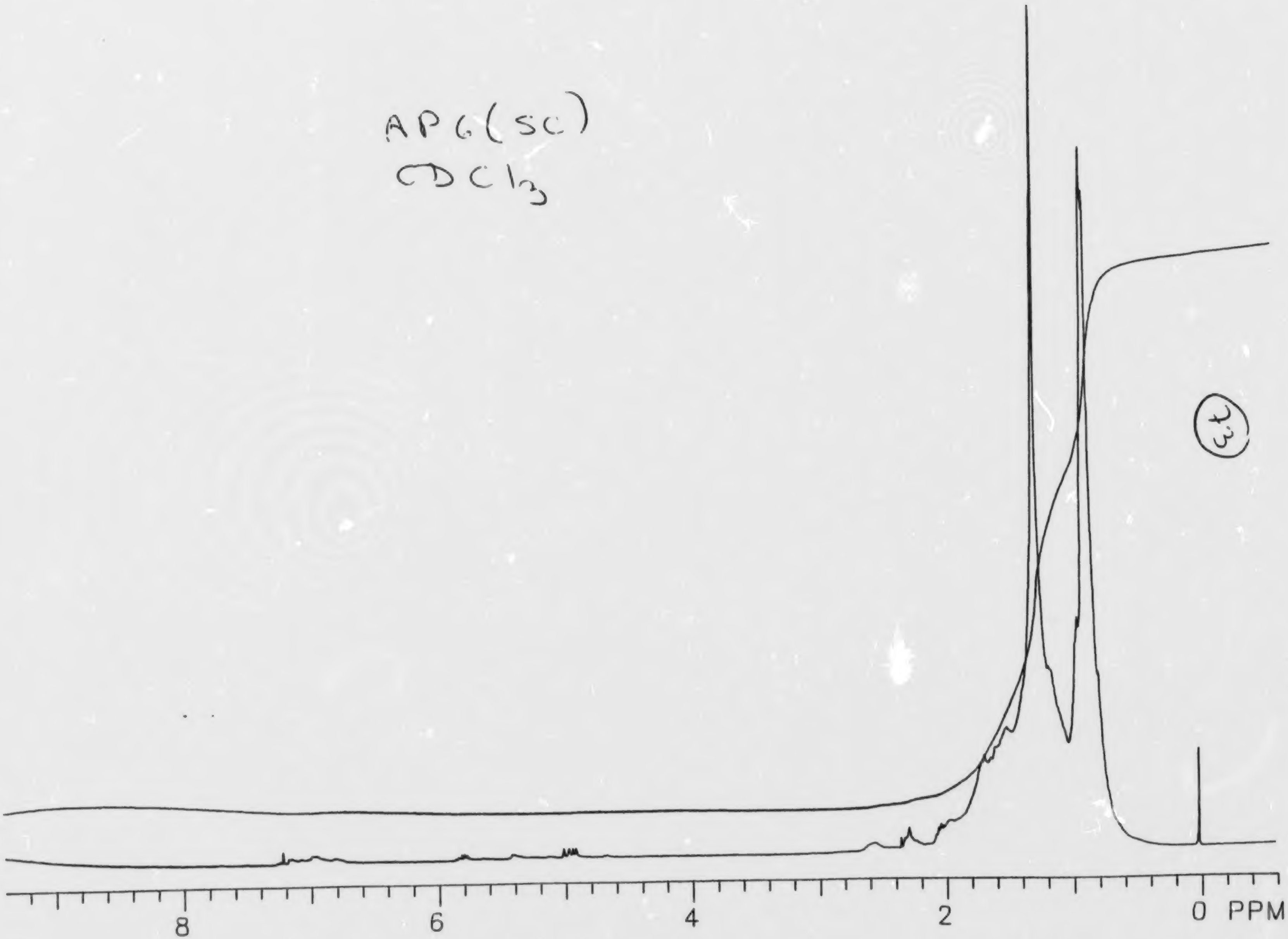
$CDCl_3$

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   44.73
  RFL=   242.3  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01  2320.51    5.803   63.511
 02  2313.85    5.787   65.726
 03  2303.54    5.761   49.416
 04  2160.56    5.403   52.765
 05  2160.01    5.402   50.791
 06  2159.67    5.401   47.863
 07  2156.81    5.394   47.442
 08  2156.39    5.393   47.704
 09  2001.99    5.007   65.359
 10  2000.52    5.003  100.772
 11  1998.99    4.999   90.158
 12  1998.62    4.998   96.418
 13  1997.01    4.994   52.917
 14  1986.04    4.967   47.883
 15  1984.90    4.964   70.828
 16  1983.34    4.960  103.519
 17  1982.61    4.958   97.812
 18  1981.41    4.955  104.745
 19  1979.80    4.951   71.712
 20  1972.20    4.932   73.721
 21  1971.10    4.929  103.648
 22  1970.13    4.927   94.302
 23  1969.08    4.924   84.540
 24  1967.62    4.921   53.788
 25  1962.22    4.907   71.193
 26  1961.00    4.904   96.962
 27  1960.29    4.902   87.853
 28  1959.93    4.901   90.623
 29  1958.90    4.899   82.307
 30  1957.58    4.896   49.423
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   44.73
  RFL=   242.3  RFP=       0
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   44.73
  RFL=   242.3  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01   504.63    1.262  139.848
 02   352.28    0.881  111.996
 03   350.50    0.877  109.425
 04   348.79    0.872  108.968
 05   344.15    0.861  111.767
 06   335.73    0.840   80.281
```

```
  ACQUISITION                                          PROCESSING
SFRQ   399.869          DATE  23-04-86          SE    NOT USED
TN       1.750          SOLVNT  CDCL3           LB    NOT USED
SW      4000.0          FILE    AP6SC           RE    NOT USED
AT       3.752                                  CD    NOT USED
NP       30016            DECOUPLING            CCD   NOT USED
FB        2200          DN       1.750          AF    NOT USED
BS          16          DO        74.5          FN       65536
SS           0          DM         NNN          MATH     F
PW         1.0          DLP         20
P1           0                                    SPECIAL
D1       1.000              FLAGS               TEMP  NOT USED
D2           0          IL         N            VTC       25.0
TO        -200          IN         N            PW90      13.0
NT          64          DP         Y
CT          64
```

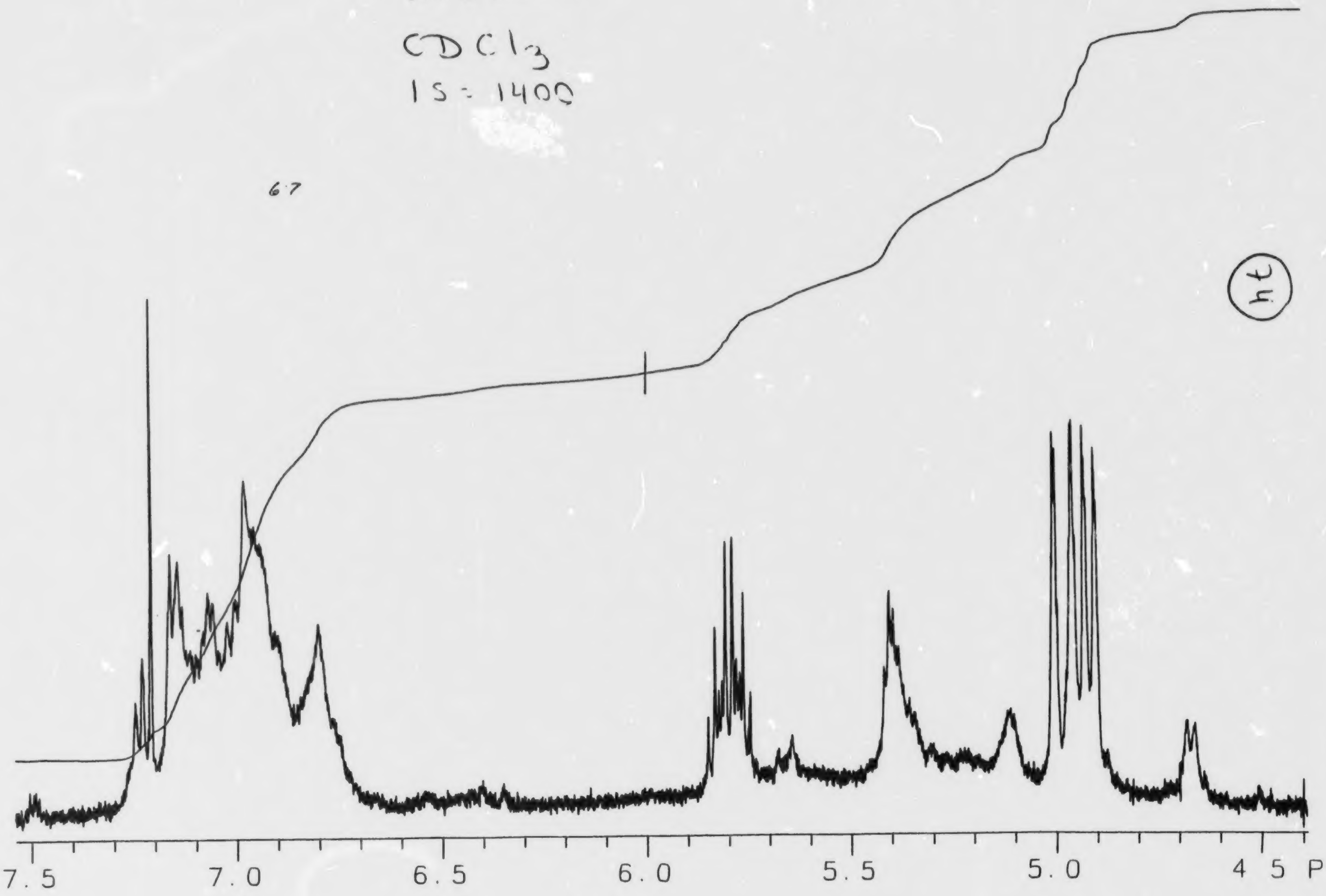


AP6(SC)
CDCl$_3$

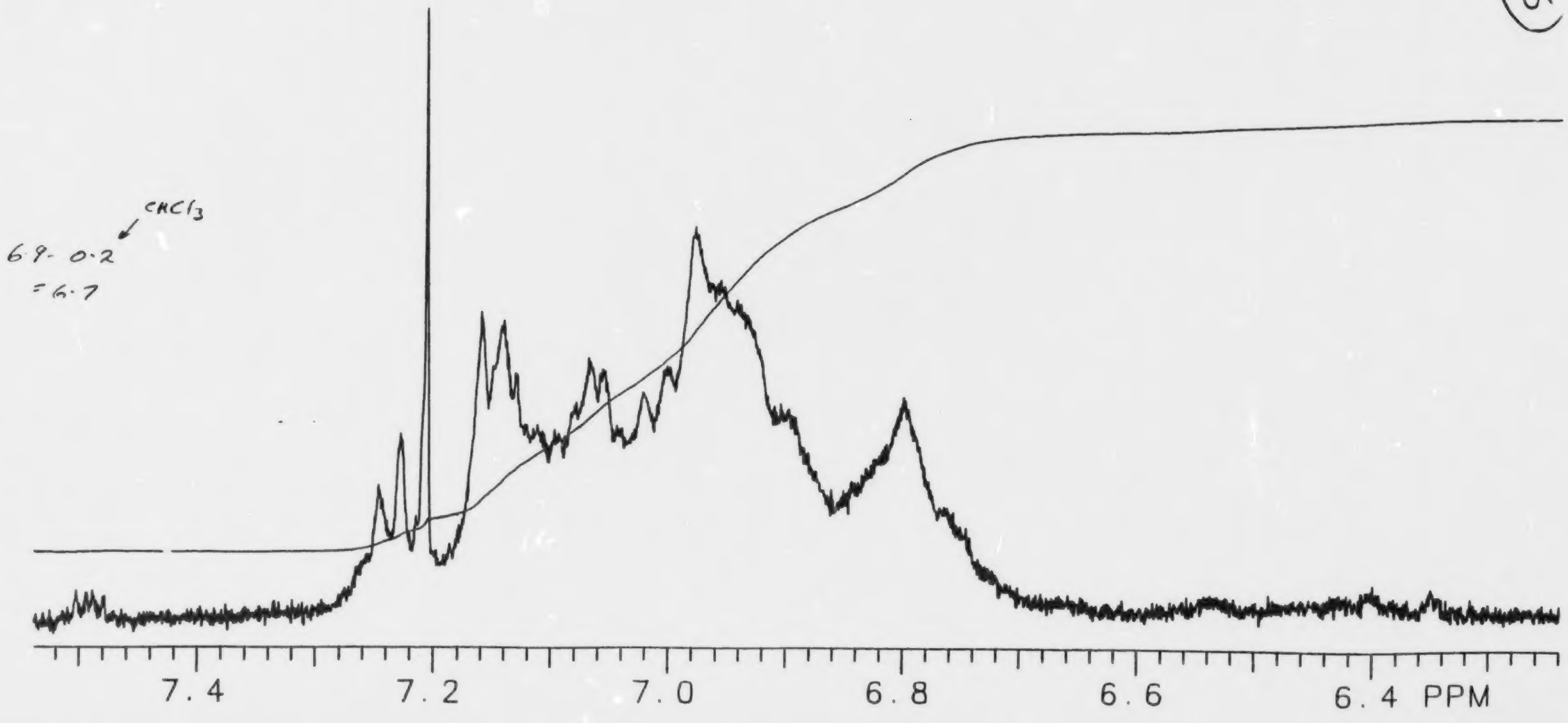
(73)

IS = 1400

AP6(SC)
$CDCl_3$
IS = 1400



Aβ6 (SC)
CDCl$_3$

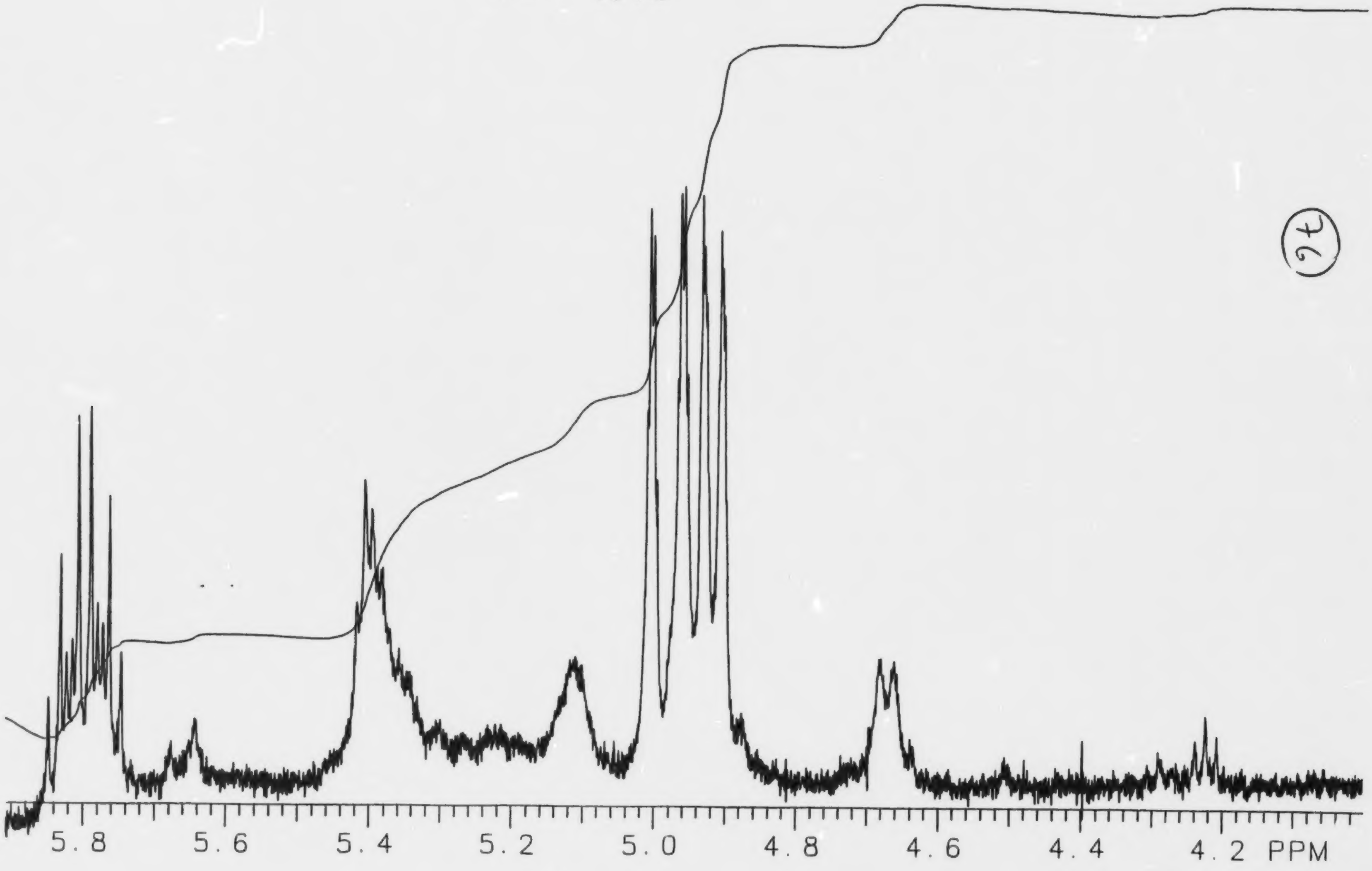


IS = 4600

AP6(SC)

$CDCl_3$

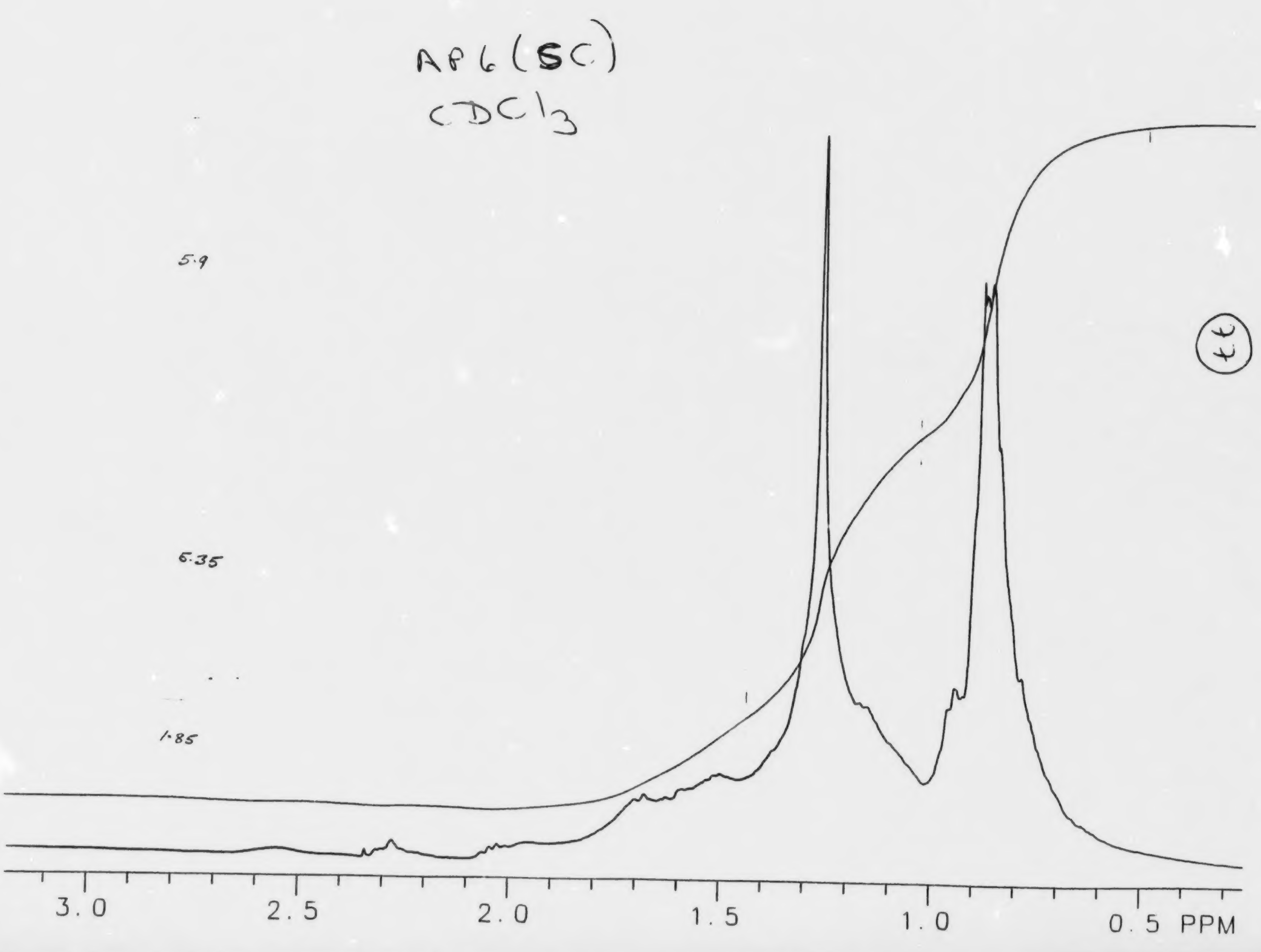
IS = 4600

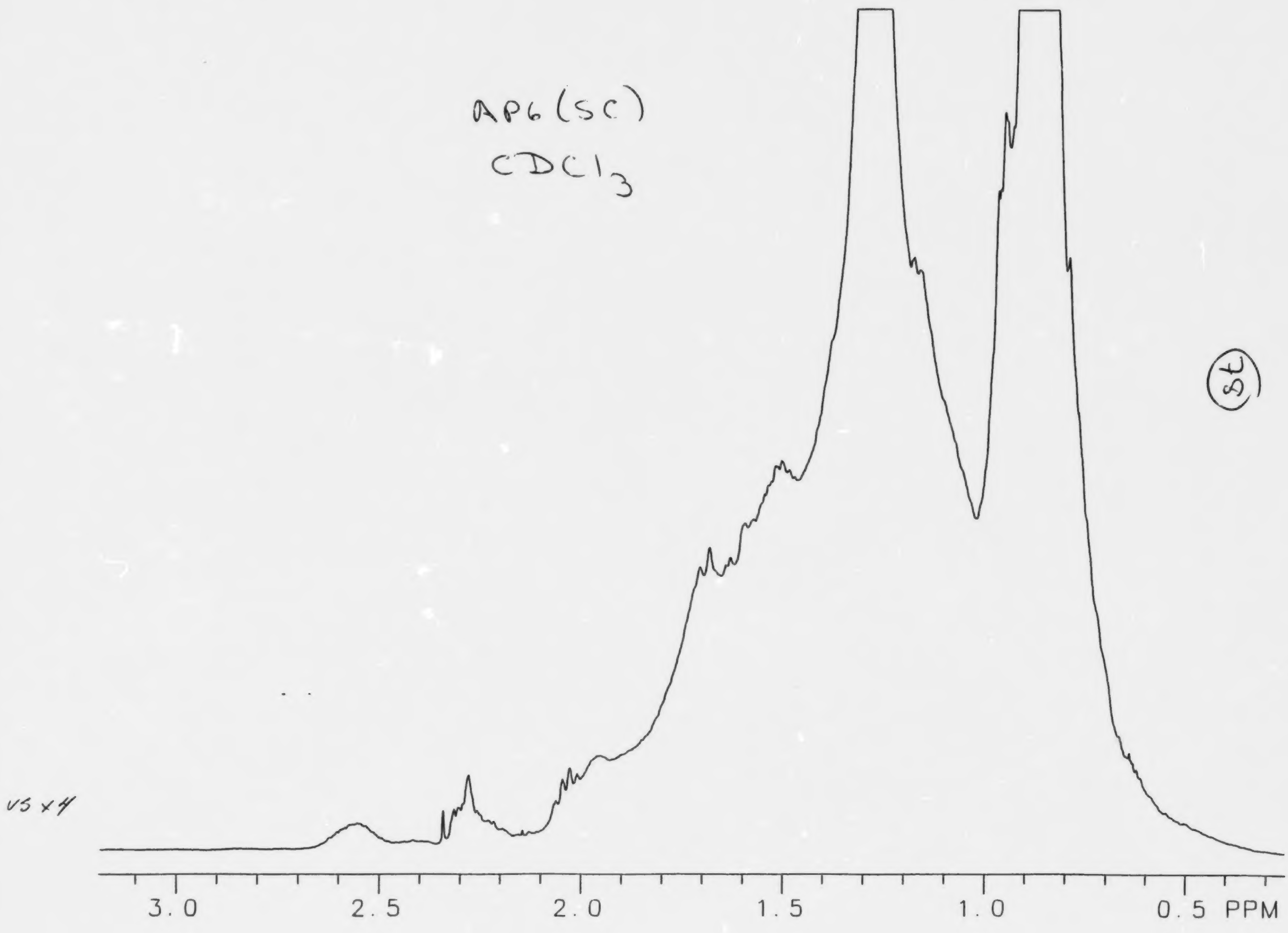


76

AP6 (SC)
$CDCl_3$

(77)




AP6 (SC)
CDCl3
VS ×4
3.0
2.5
2.0
1.5
1.0
0.5 PPM

AP73C

$CDCl_3$

(79)

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=    9.20
  RFL=   243.2  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01  2899.63    7.251   37.158
 02  2898.04    7.247   20.091
 03  2892.82    7.234   76.230
 04  2892.03    7.232   85.474
 05  2886.81    7.219   32.365
 06  2884.98    7.215   86.829
 07  2880.00    7.202   14.686
 08  2864.74    7.164  100.123
 09  2864.13    7.163  100.125
 10  2862.06    7.157   44.817
 11  2861.23    7.155   54.811
 12  2860.83    7.154   51.608
 13  2859.78    7.152   42.546
 14  2859.25    7.150   43.918
 15  2858.15    7.148   57.240
 16  2857.54    7.146   68.488
 17  2856.75    7.144   72.232
 18  2856.24    7.143   63.458
 19  2855.22    7.140   49.077
 20  2854.36    7.138   35.474
 21  2853.02    7.135   45.526
 22  2850.55    7.129   12.121
 23  2850.09    7.128   10.675
 24  2847.23    7.120   10.413
 25  2846.65    7.119   12.421
 26  2845.74    7.117   15.572
 27  2845.33    7.116   14.626
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   20.91
  RFL=   243.2  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01  2339.70    5.851   21.554
 02  2332.96    5.834   45.279
 03  2329.39    5.825   27.077
 04  2326.22    5.817   28.079
 05  2322.70    5.809   68.595
 06  2315.99    5.792   70.444
 07  2312.33    5.783   31.595
 08  2309.15    5.775   31.416
 09  2305.76    5.766   53.046
 10  2299.02    5.749   27.009
```

```
13  2162.18     5.407   62.382
14  2160.32     5.403   38.353
15  2158.27     5.397   50.671
16  2157.08     5.394   42.066
17  2156.17     5.392   32.791
18  2155.61     5.391   31.255
19  2155.07     5.389   32.651
20  2153.36     5.385   35.804
21  2152.93     5.384   36.233
22  2152.53     5.383   34.310
23  2150.85     5.379   24.281
24  2150.49     5.378   24.761
25  2150.12     5.377   23.673
26  2149.51     5.376   22.749
27  2148.75     5.374   23.480
28  2148.26     5.372   24.158
29  2003.45     5.010   48.725
30  2001.87     5.006   89.493
31  1999.82     5.001   88.868
32  1998.23     4.997   47.896
33  1989.20     4.975   21.479
34  1987.98     4.972   25.230
35  1986.39     4.968   50.673
36  1984.80     4.964   88.647
37  1982.76     4.959   88.968
38  1980.96     4.954   59.814
39  1973.69     4.936   56.143
40  1972.47     4.933   87.618
41  1971.38     4.930   75.767
42  1970.25     4.927   72.648
43  1969.23     4.925   43.250
44  1965.79     4.916   22.101
45  1963.59     4.911   54.036
46  1962.37     4.908   83.128
47  1961.24     4.905   72.994
48  1960.14     4.902   68.855
49  1958.90     4.899   38.153
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   16.11
  RFL=   243.2  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01    935.92    2.341   38.179
 02    520.80    1.302   21.620
 03    504.75    1.262  151.847
 04    359.41    0.899   32.487
 05    352.52    0.882   72.434
 06    350.33    0.876   38.069
 07    348.79    0.872   35.223
 08    345.56    0.864   42.437
 09    343.79    0.860   31.841
 10    342.69    0.857   31.327
 11    342.02    0.855   32.833
 12    335.36    0.839   16.940
```

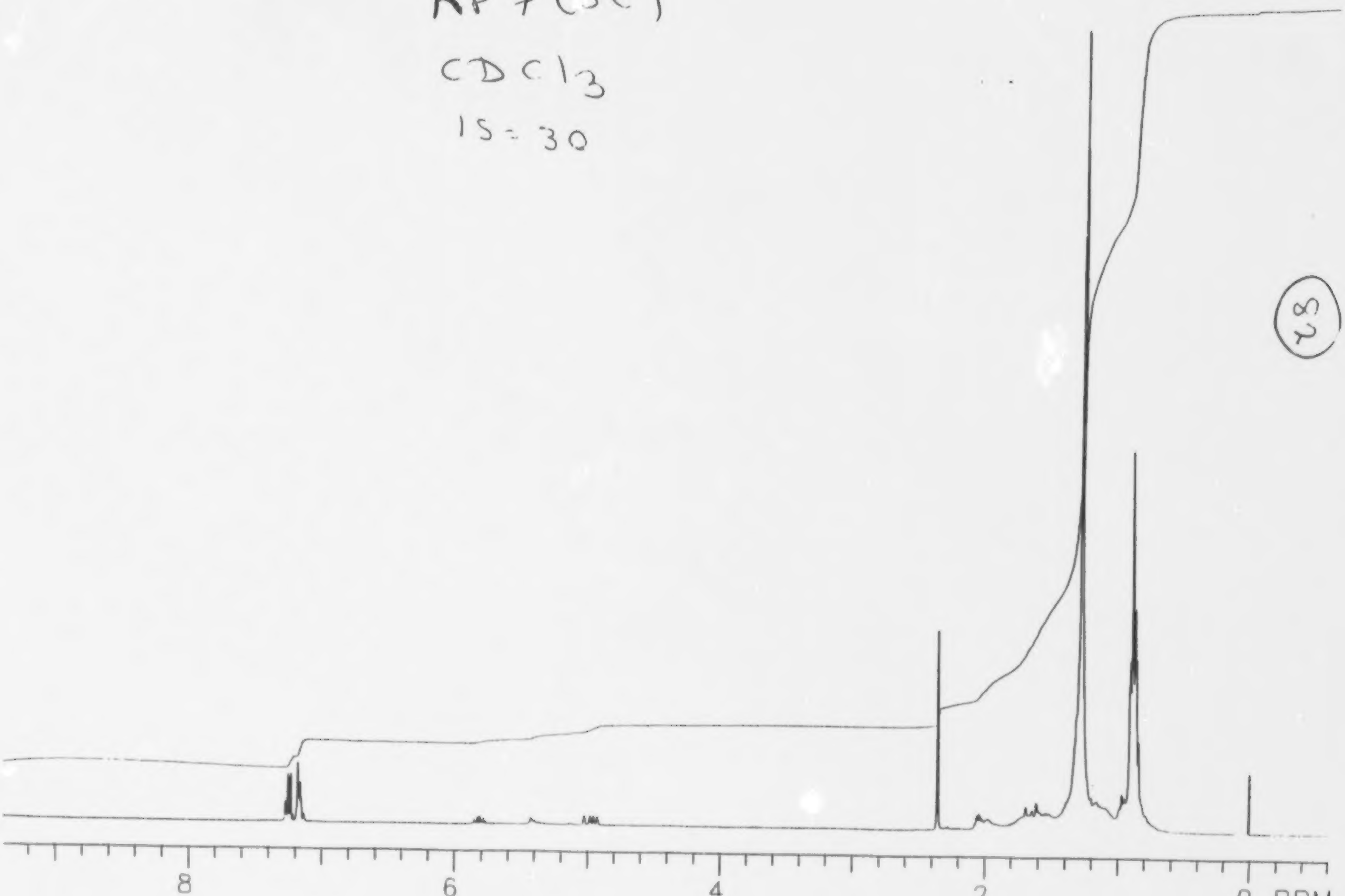
(81)

```
  ACQUISITION                                      PROCESSING
SFRQ   399.869        DATE  23-04-86           SE     NOT USED
TN       1.750        SOLVNT  CDCL3            LB     NOT USED
SW      4000.0        FILE    AP7SC            RE     NOT USED
AT       3.752                                 CD     NOT USED
NP       30016           DECOUPLING            CCD    NOT USED
FB        2200        DN          1.750        AF     NOT USED
BS          16        DO           74.5        FN        65536
SS           0        DM            NNN        MATH      F
PW         1.0        DLP            20
P1           0                                    SPECIAL
D1       1.000            FLAGS                TEMP   NOT USED
D2           0        IL          N            VTC        25.0
TO        -200        IN          N            PW90       13.0
NT          48        DP          Y
CT          48
```

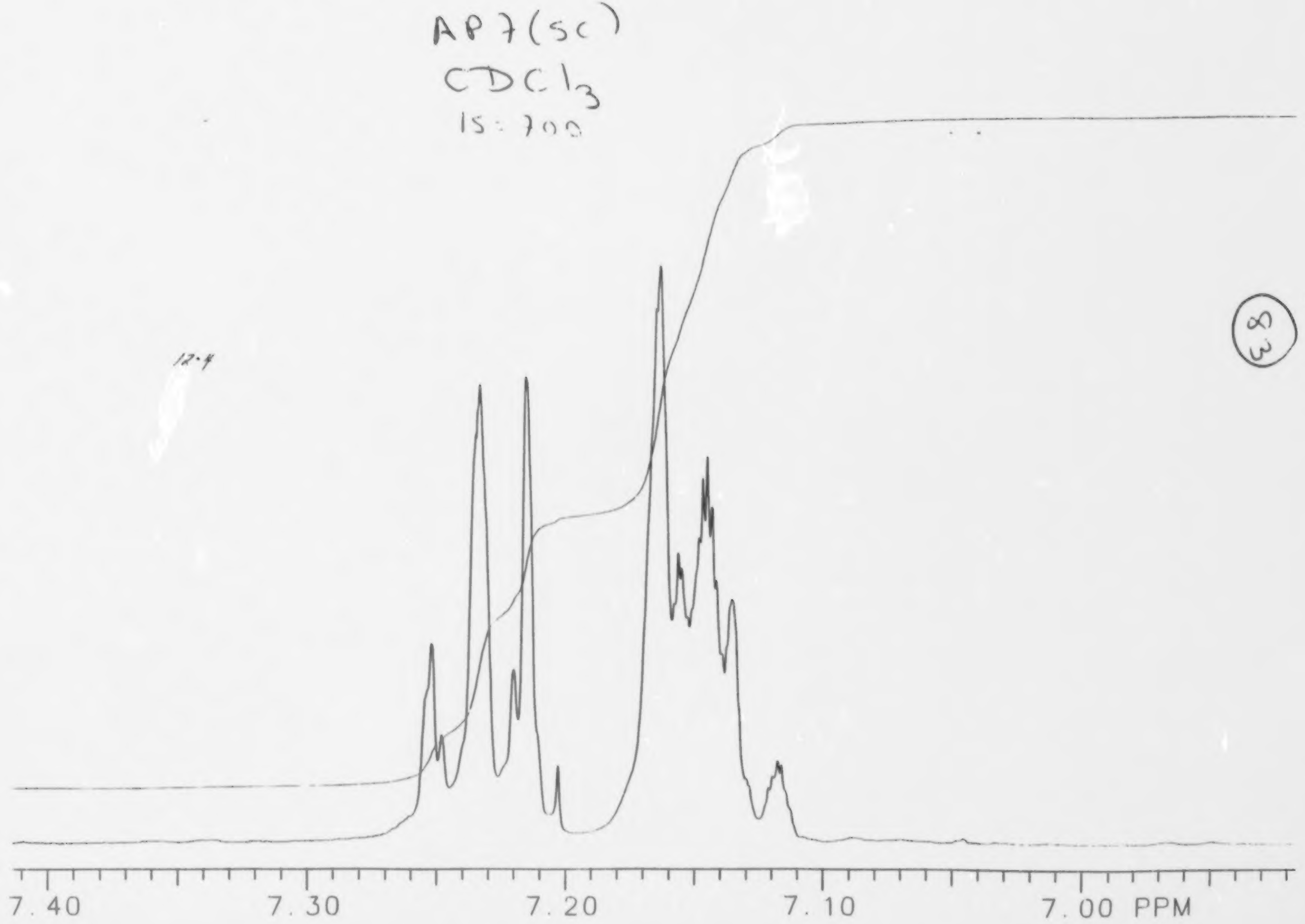
IS=30

AP7 (SC)
$CDCl_3$
IS = 30

82



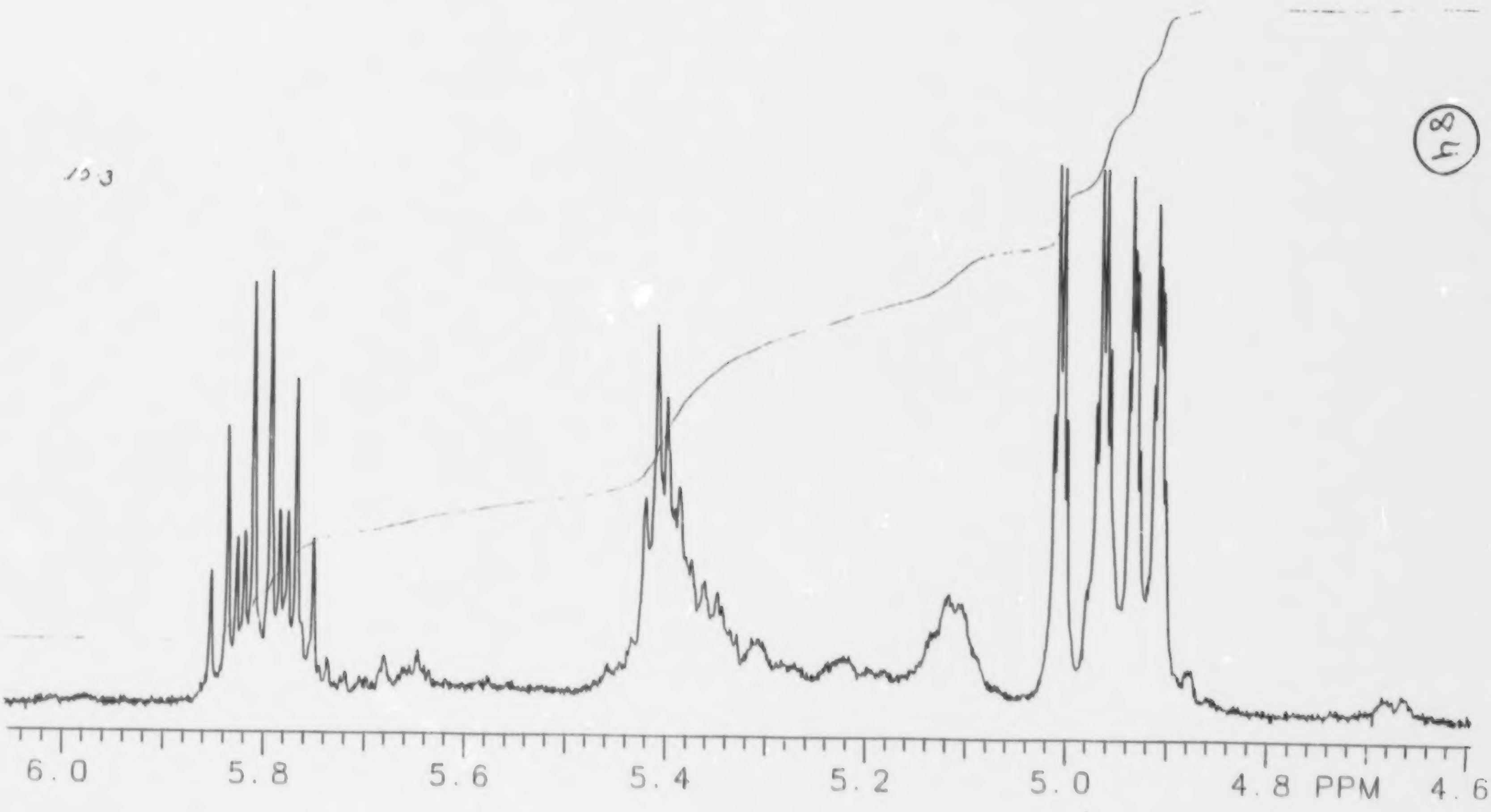
IS=700



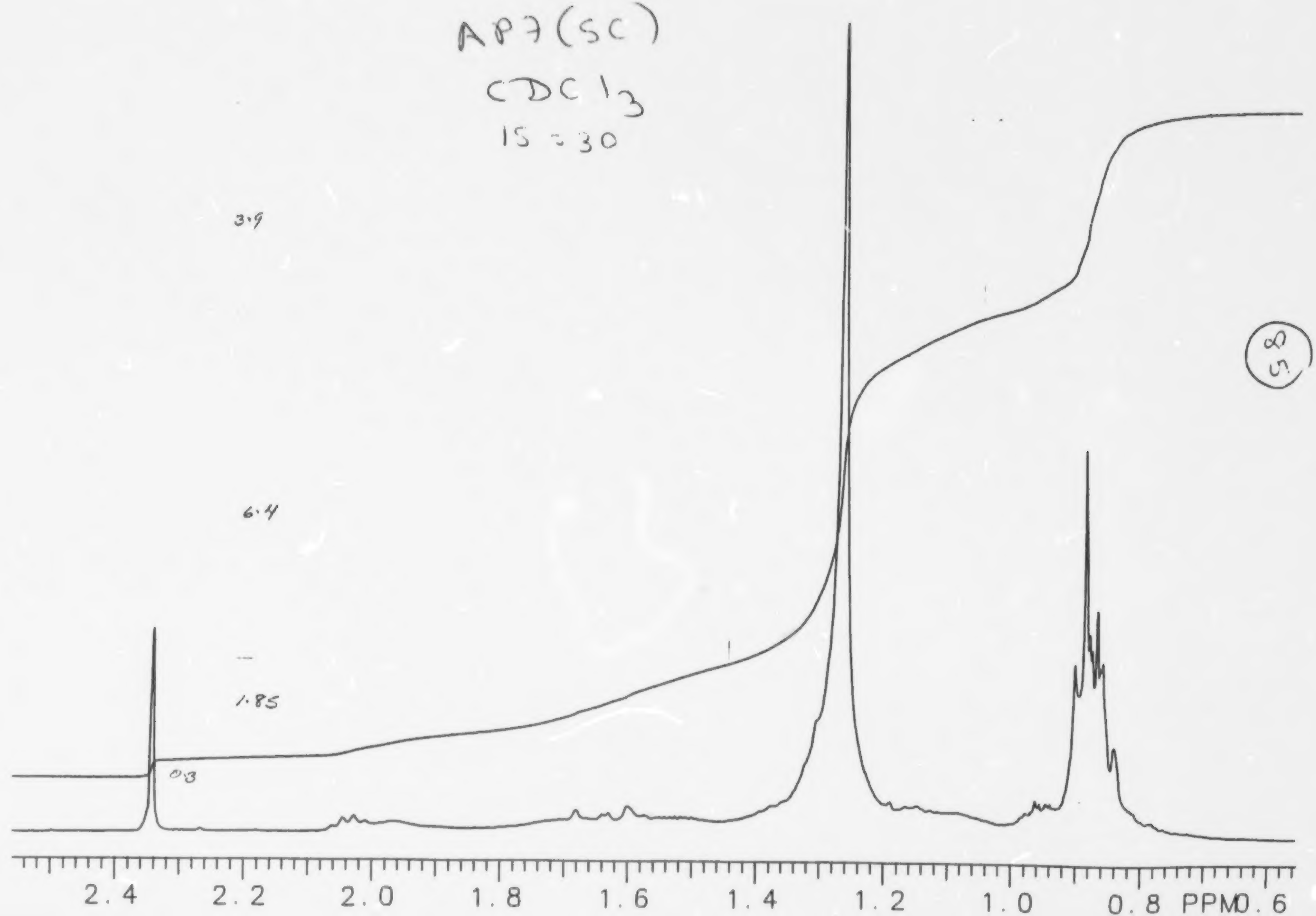
IS=1000

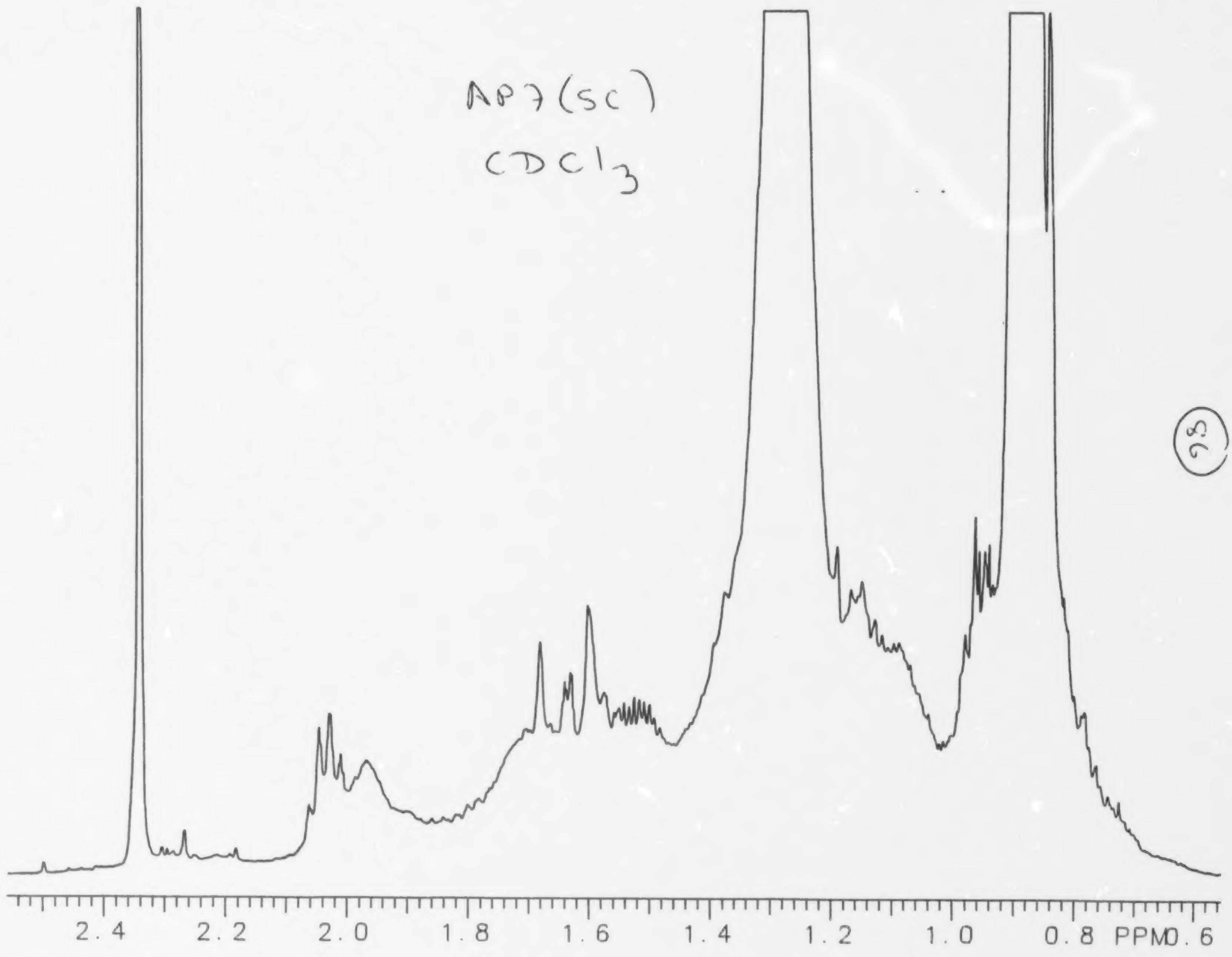
AP7(SC)
CDCl$_3$
IS=1000

(84)



IS = 30





98

(87)

HB 1B

1-5-86

$CDCl_3$

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   25.57
  RFL=   242.4  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01  1449.54    3.625   31.937
 02  1448.90    3.623   27.587
 03  1442.92    3.608   56.997
 04  1436.23    3.592   33.069
 05  1396.13    3.491   47.816
 06  1389.20    3.474  139.467
 07  1382.10    3.456  139.732
 08  1375.17    3.439   47.322
```

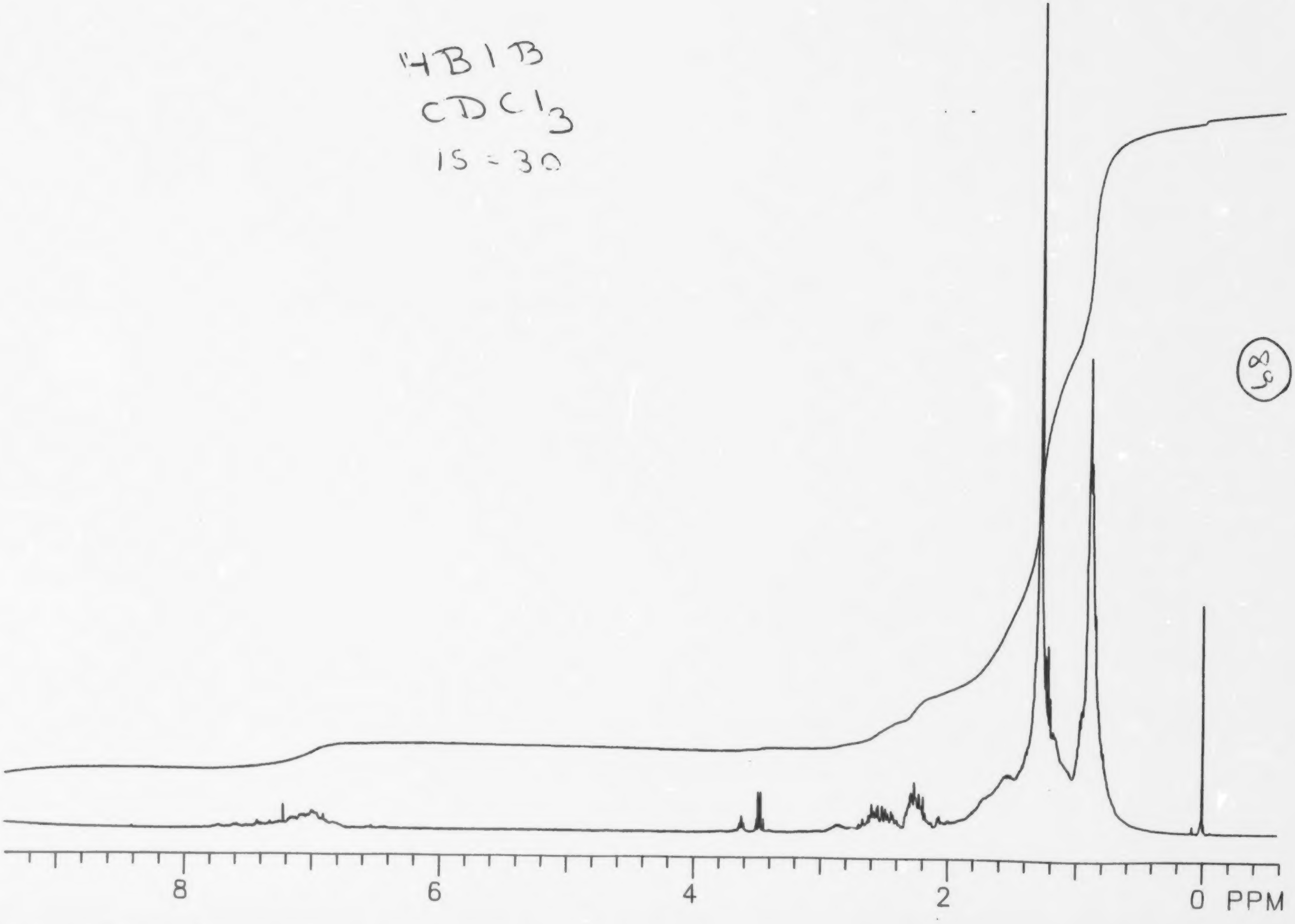
```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   24.36
  RFL=   242.4  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01    519.28   1.299   32.942
 02    518.48   1.297   32.972
 03    503.04   1.258  159.019
 04    487.44   1.219   34.017
 05    480.51   1.202   35.971
 06    473.40   1.184   25.957
 07    368.45   0.921   24.634
 08    368.08   0.921   24.700
 09    366.98   0.918   25.240
 10    365.83   0.915   25.584
 11    358.56   0.897   51.620
 12    357.53   0.894   51.408
 13    351.91   0.880   90.995
 14    349.77   0.875   72.351
 15    348.06   0.870   69.960
 16    345.01   0.863   70.959
 17    343.30   0.859   66.195
 18    341.47   0.854   64.571
 19    334.63   0.837   41.991
 20    333.72   0.835   41.704
```

(88)

```
  ACQUISITION                                   PROCESSING
SFRQ   399.869     DATE  01-05-86          SE    NOT USED
TN       1.750     SOLVNT  CDCL3           LB    NOT USED
SW      4000.0     FILE     HB1B           RE    NOT USED
AT       3.752                             CD    NOT USED
NP       30016        DECOUPLING           CCD   NOT USED
FB        2200     DN         1.750        AF    NOT USED
BS          16     DO          74.5        FN       65536
SS           0     DM           NNN        MATH     F
PW         1.0     DLP           20
P1           0                                SPECIAL
D1       1.000          FLAGS              TEMP  NOT USED
D2           0     IL          N           VTC       25.0
TO        -200     IN          N           PW90      13.0
NT          32     DP          Y
CT          32
```

IS = 30

¹HB1B
$CDCl_3$
IS = 30



(89)

IS = 600

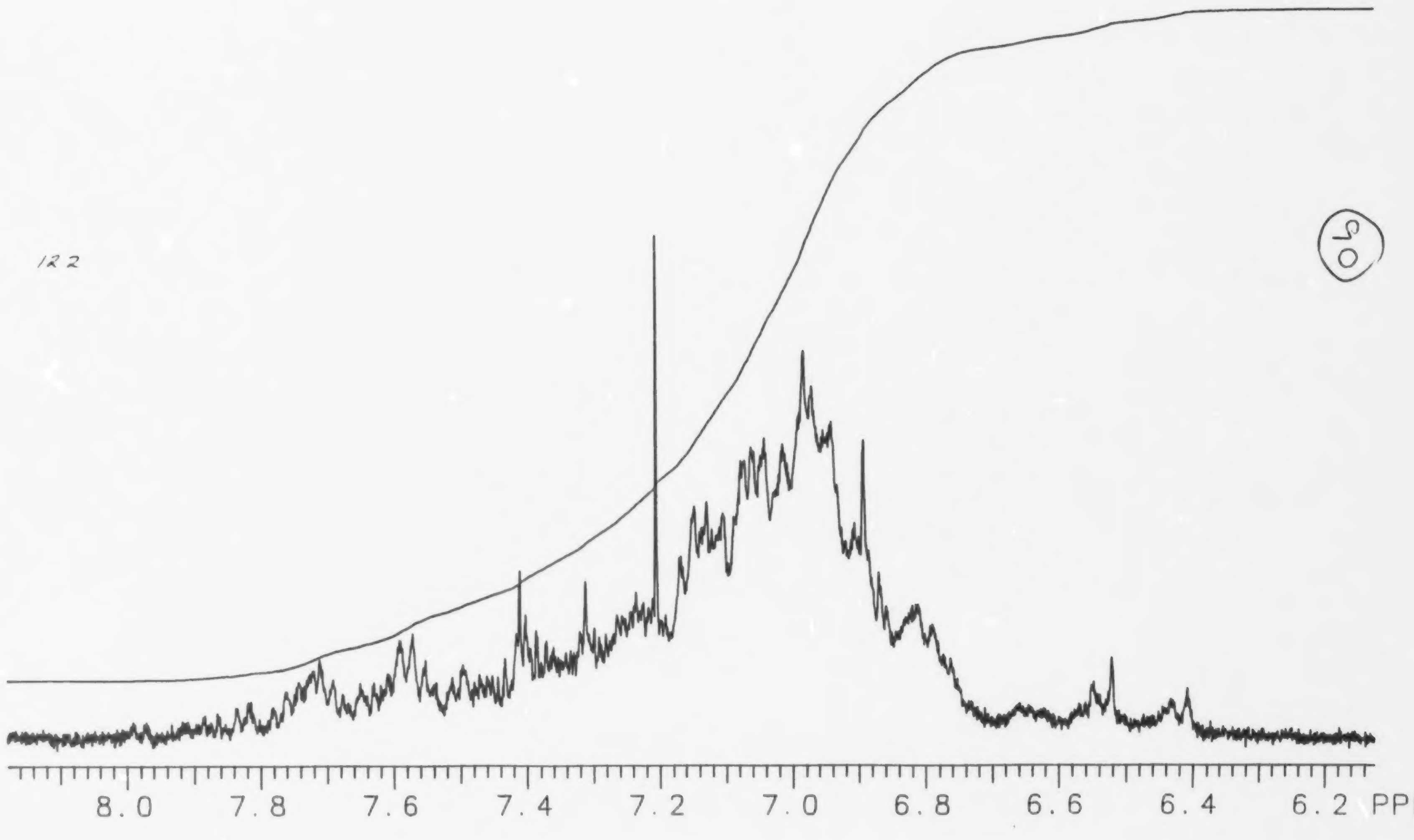
HB 1B

$CDCl_3$

IS = 600

(90)

122



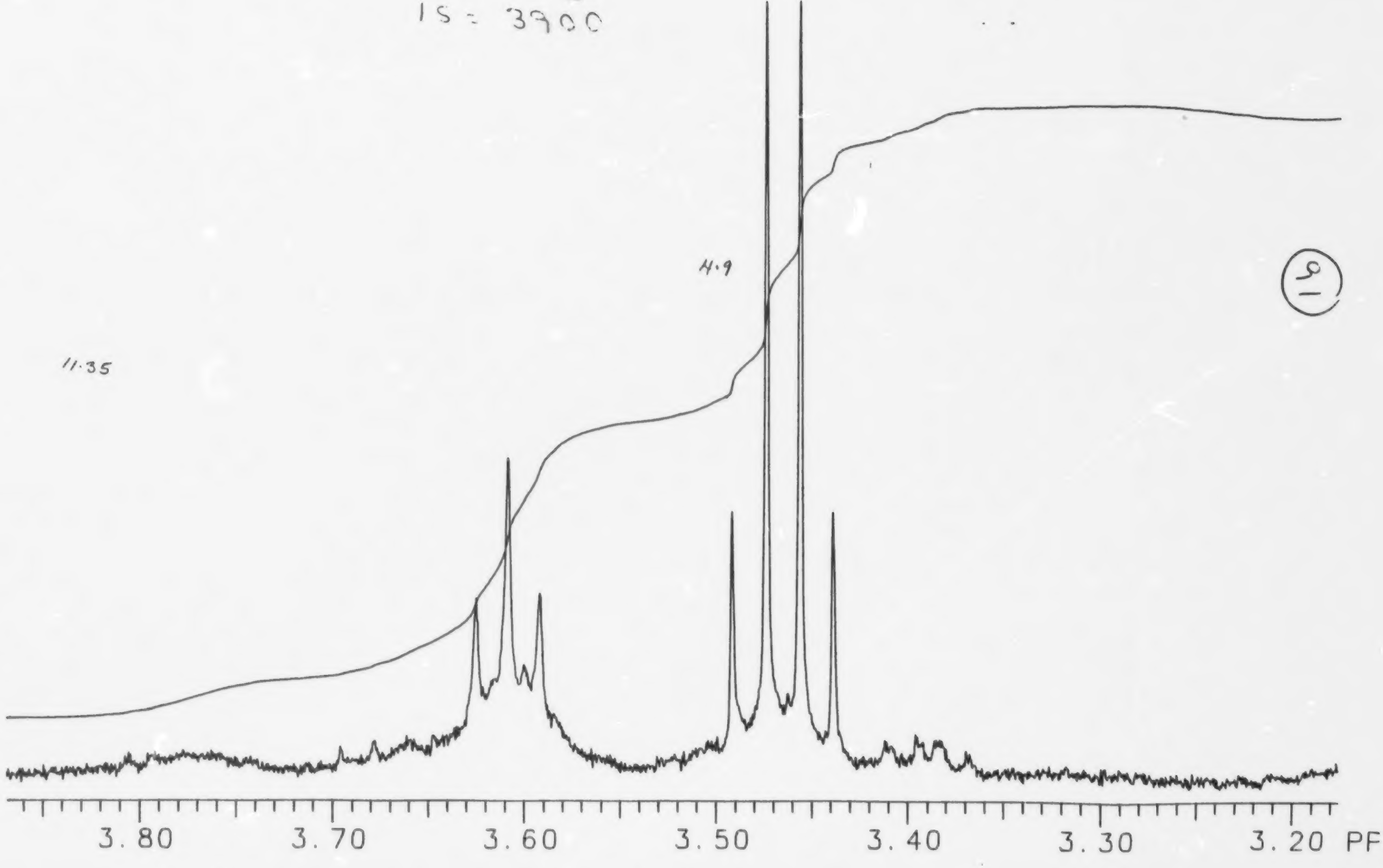
IS = 3900

HB1B

$CDCl_3$

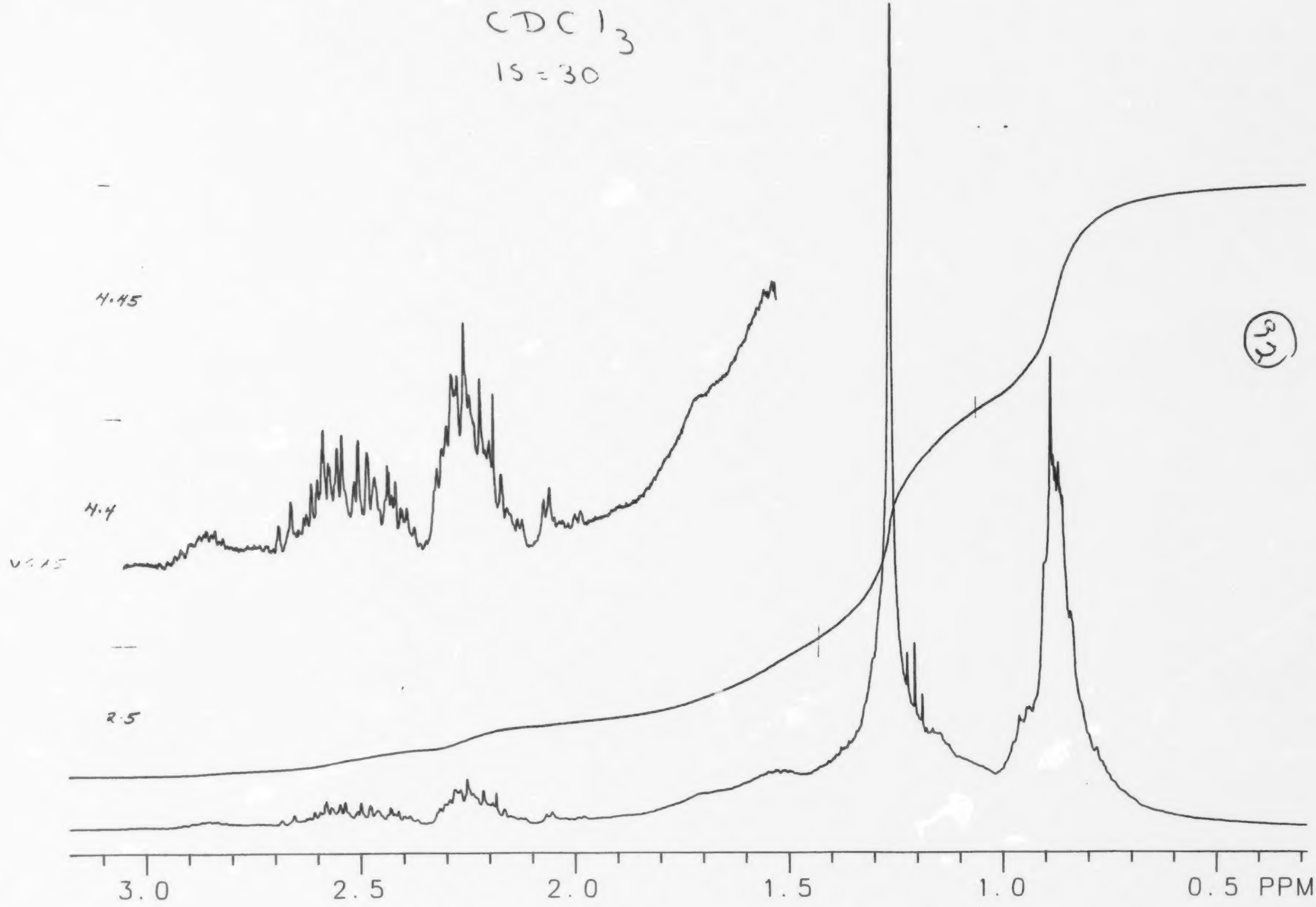
IS = 3900

91



IS=30

HB1B
CDCl$_3$
IS=30



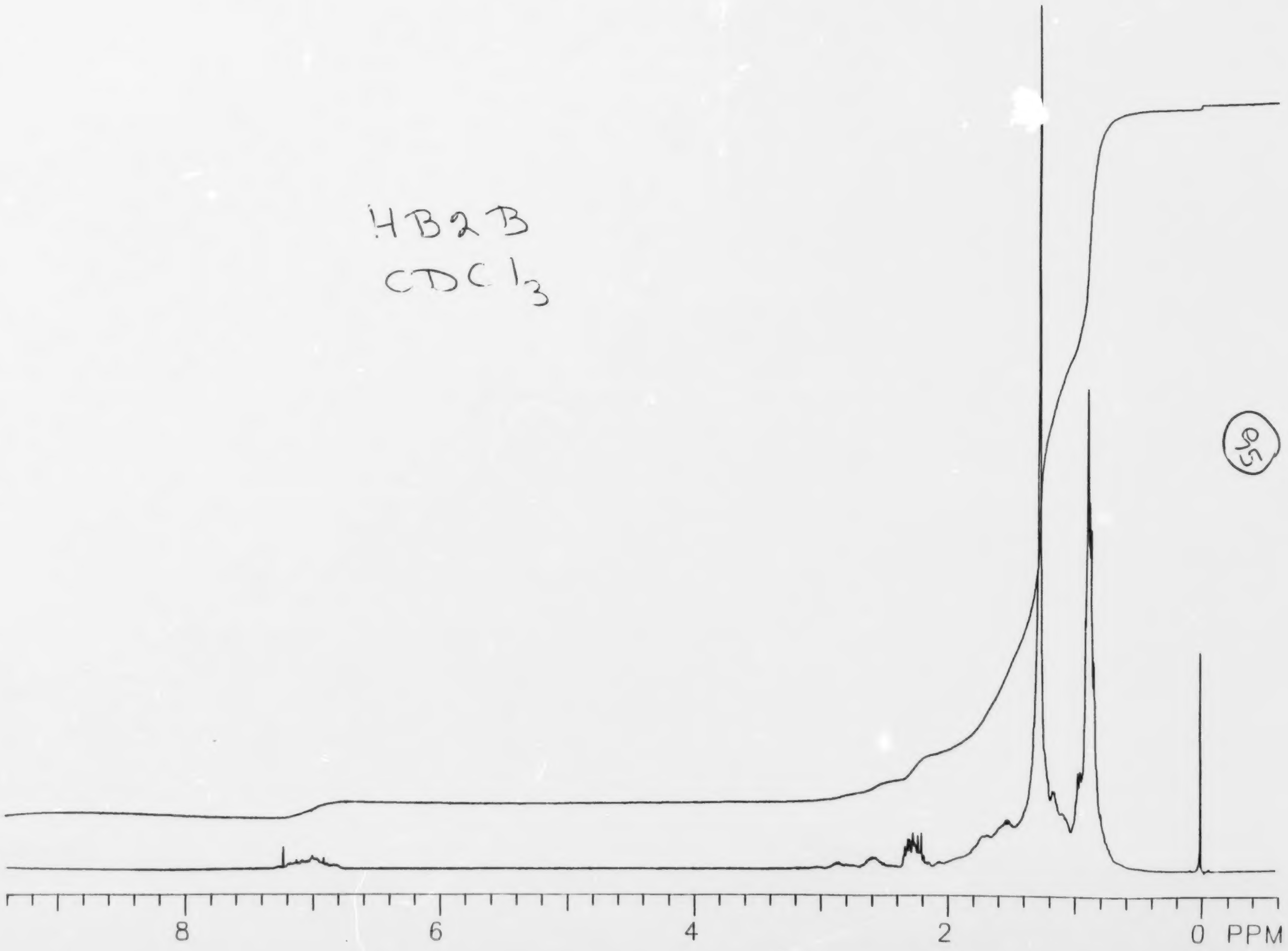
(93) HB2R 1-5-86
$CDCl_3$

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   29.15
  RFL=   240.6  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01    504.14    1.261  150.047
 02    359.05    0.898   43.253
 03    352.28    0.881   83.438
 04    350.14    0.876   65.128
 05    348.25    0.871   63.770
 06    345.32    0.864   61.619
 07    343.54    0.859   58.504
 08    341.69    0.854   59.400
 09    334.88    0.837   36.432
 10    334.02    0.835   36.155
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   19.26
  RFL=   240.6  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01    927.18    2.319   19.456
 02    917.85    2.295   25.942
 03    911.26    2.279   25.406
 04    908.33    2.272   23.712
 05    907.96    2.271   23.560
 06    902.96    2.258   21.717
 07    901.52    2.255   31.383
 08    900.57    2.252   27.746
 09    896.00    2.241   22.866
 10    894.41    2.237   19.714
 11    893.98    2.236   20.016
 12    893.24    2.234   20.104
 13    892.27    2.231   21.540
 14    886.65    2.217   29.192
 15    874.78    2.188   31.204
```

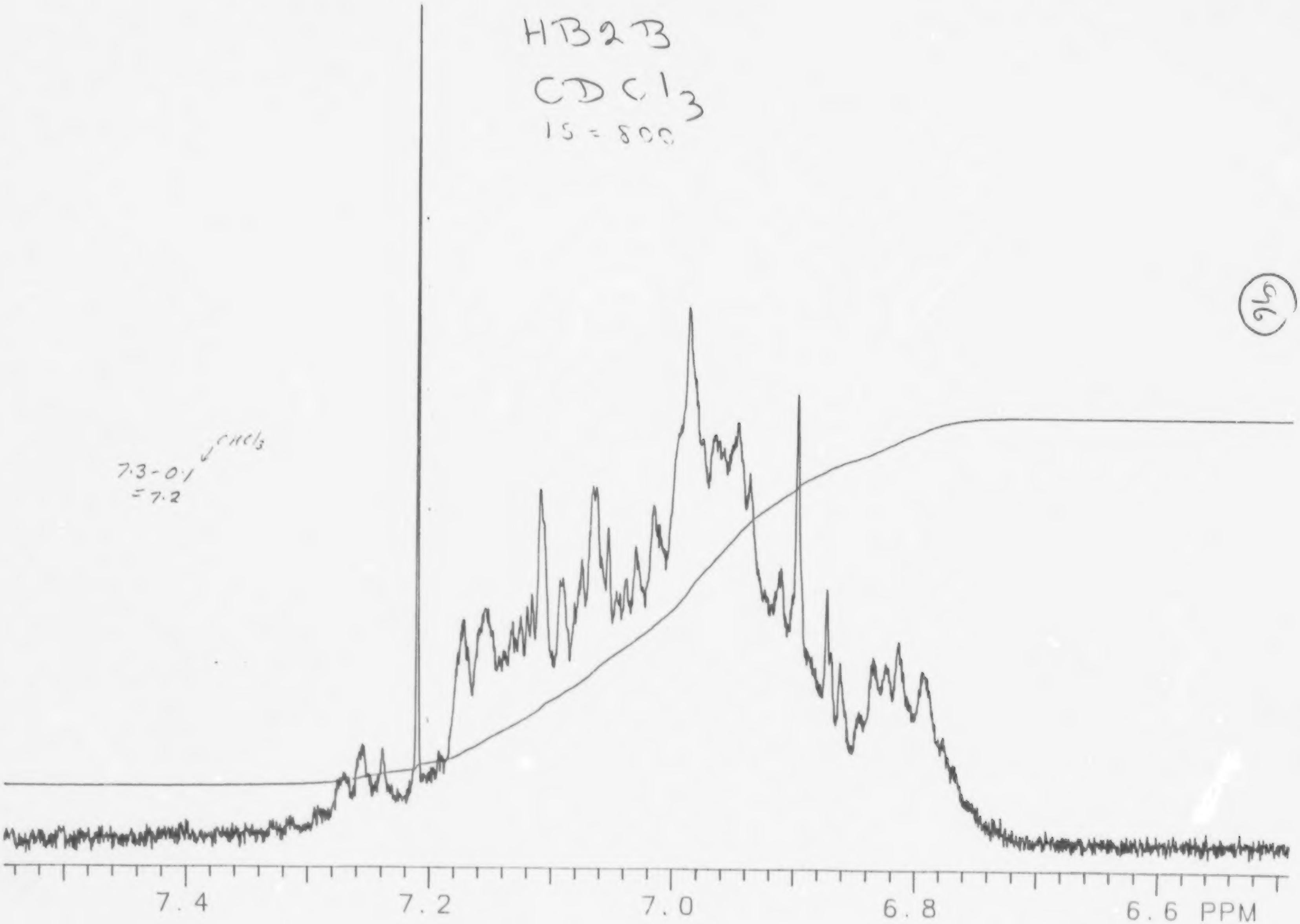
ACQUISITION PROCESSING

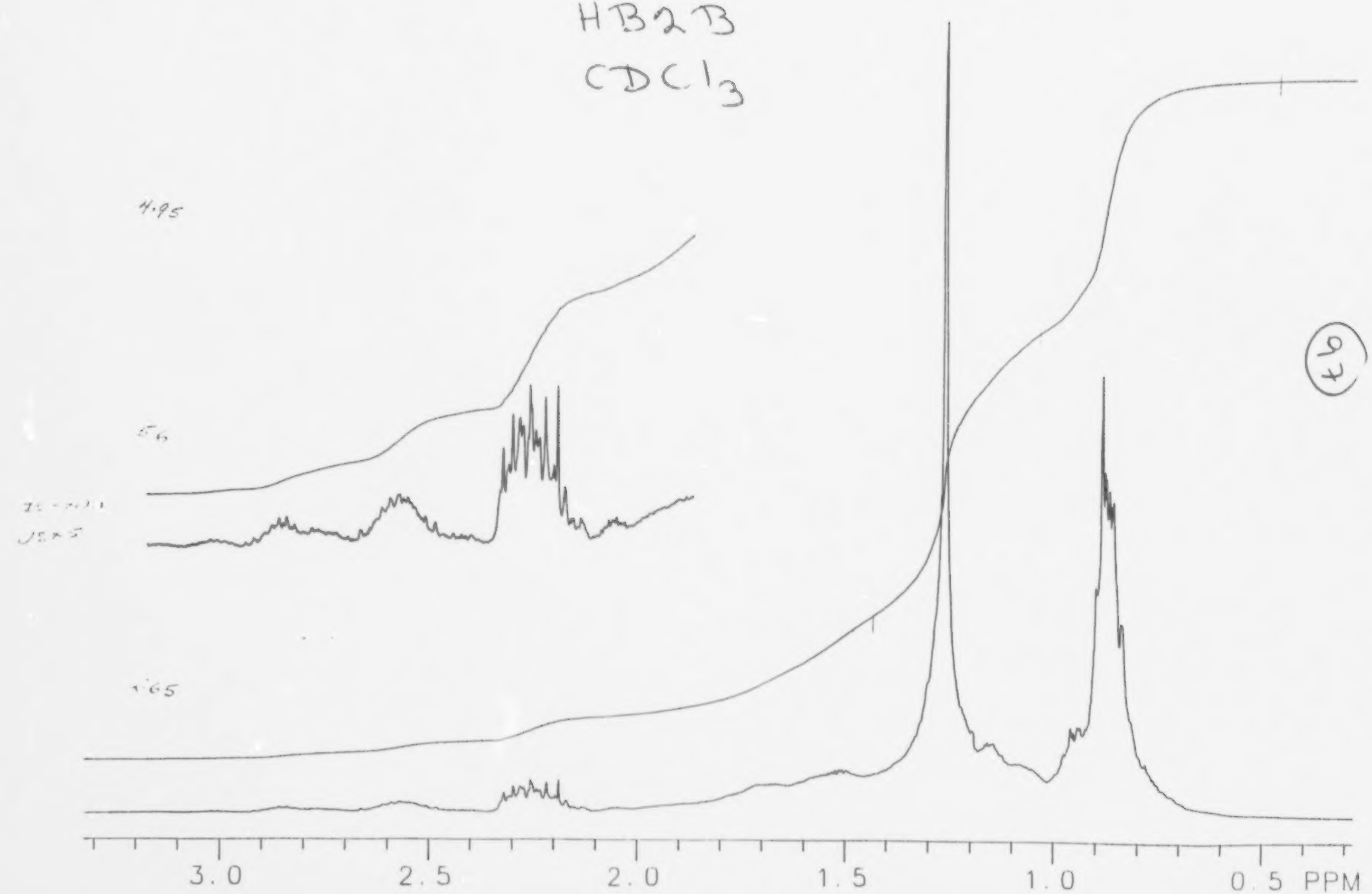
```
  ACQUISITION                                      PROCESSING
SFRQ   399.869       DATE  01-05-86          SE     NOT USED
TN       1.750       SOLVNT  CDCL3           LB     NOT USED
SW      4000.0       FILE    HB1B            RE     NOT USED
AT       3.752                               CD     NOT USED
NP       30016          DECOUPLING           CCD    NOT USED
FB        2200       DN         1.750        AF     NOT USED
BS          16       DO          74.5        FN        65536
SS           0       DM          NNN         MATH     F
PW         1.0       DLP           20
P1           0                                  SPECIAL
D1       1.000            FLAGS              TEMP  NOT USED
D2           0       IL         N            VTC        25.0
TO        -200       IN         N            PW90       13.0
NT          32       DP         Y
CT          32
```



HB2B
$CDCl_3$

(95)


HB2B
$CDCl_3$
IS = 800
7.3-0.1
= 7.2
$CHCl_3$
7.4
7.2
7.0
6.8
6.6 PPM


HB2B
CDCl3
4.95
56
1.65
(97)
3.0
2.5
2.0
1.5
1.0
0.5 PPM

HC 3A 1-5-86

(98) EXTRA

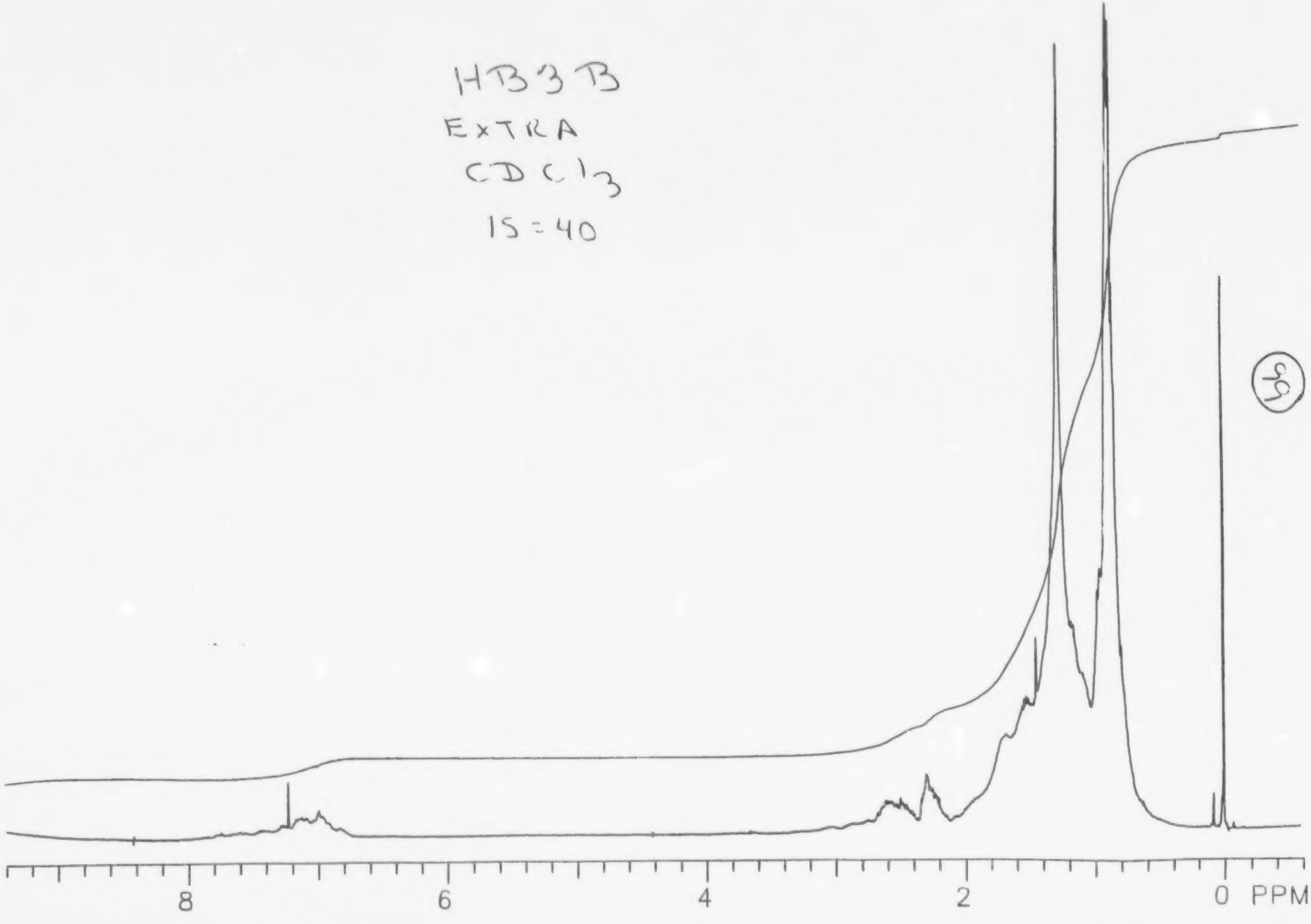
CDCl3

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   08.07
  RFL=   241.0  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01    503.34    1.259  142.847
 02    351.91    0.880  137.518
 03    349.59    0.874  150.151
 04    348.06    0.870  137.817
 05    346.23    0.866  133.618
 06    345.25    0.863  132.818
 07    343.00    0.858  146.974
 08    341.47    0.854  140.361
 09    334.51    0.837   99.321
```

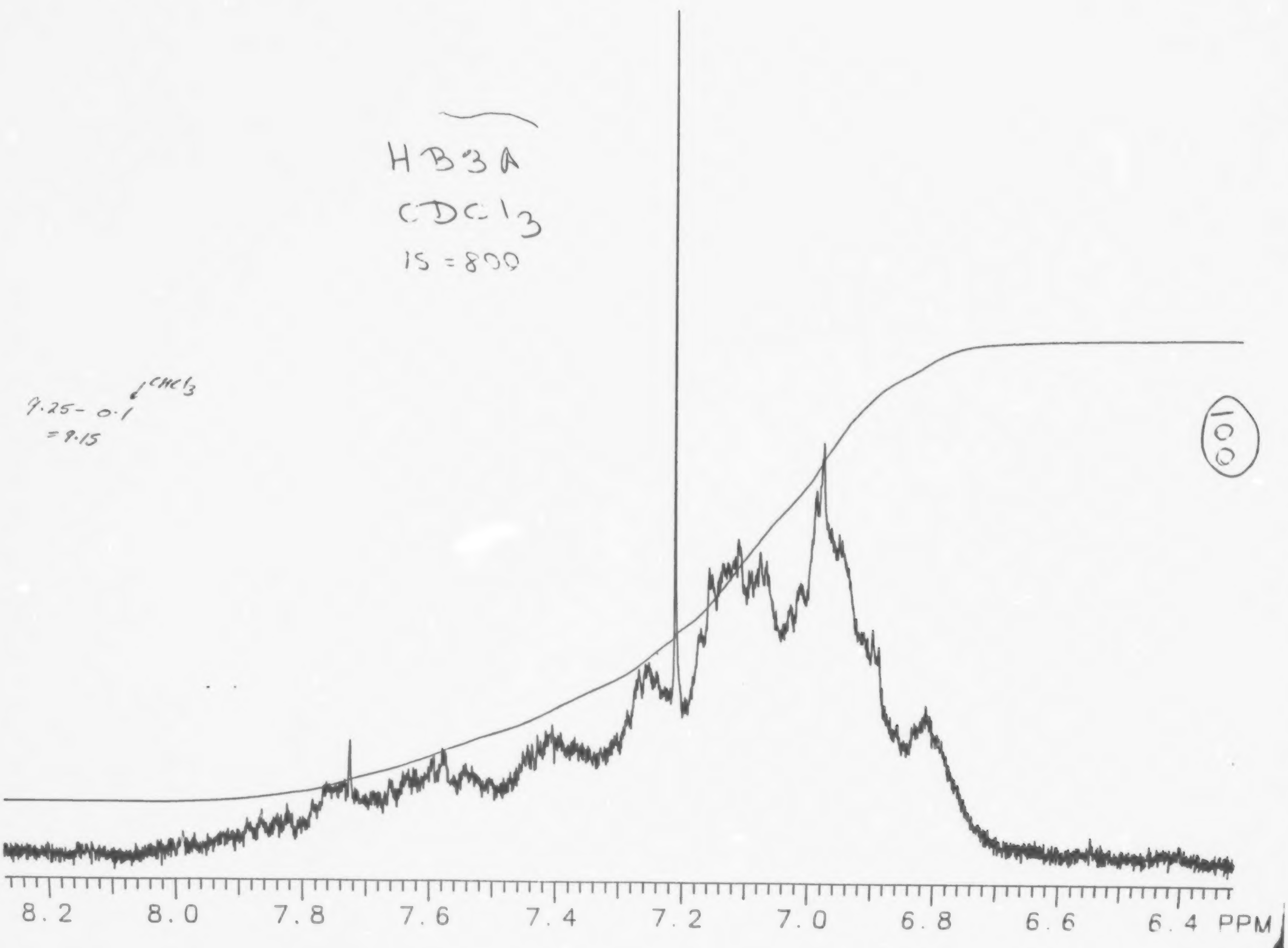
```
  ACQUISITION                                          PROCESSING
SFRQ   399.869          DATE  01-05-86            SE     NOT USED
TN       1.750          SOLVNT  CDCL3             LB     NOT USED
SW      4000.0          FILE    HB3A              RE     NOT USED
AT       3.752                                    CD     NOT USED
NP       30016             DECOUPLING             CCD    NOT USED
FB        2200          DN         1.750          AF     NOT USED
BS          16          DO          74.5          FN        65536
SS           0          DM         NNN            MATH     F
PW         1.0          DLP           20
P1           0                                       SPECIAL
D1       1.000               FLAGS                TEMP   NOT USED
D2           0          IL         N              VTC        25.0
TO        -200          IN         N              PW90       13.0
NT          48          DP         Y
CT          48
```

IS=40

(99)



ZS = 800

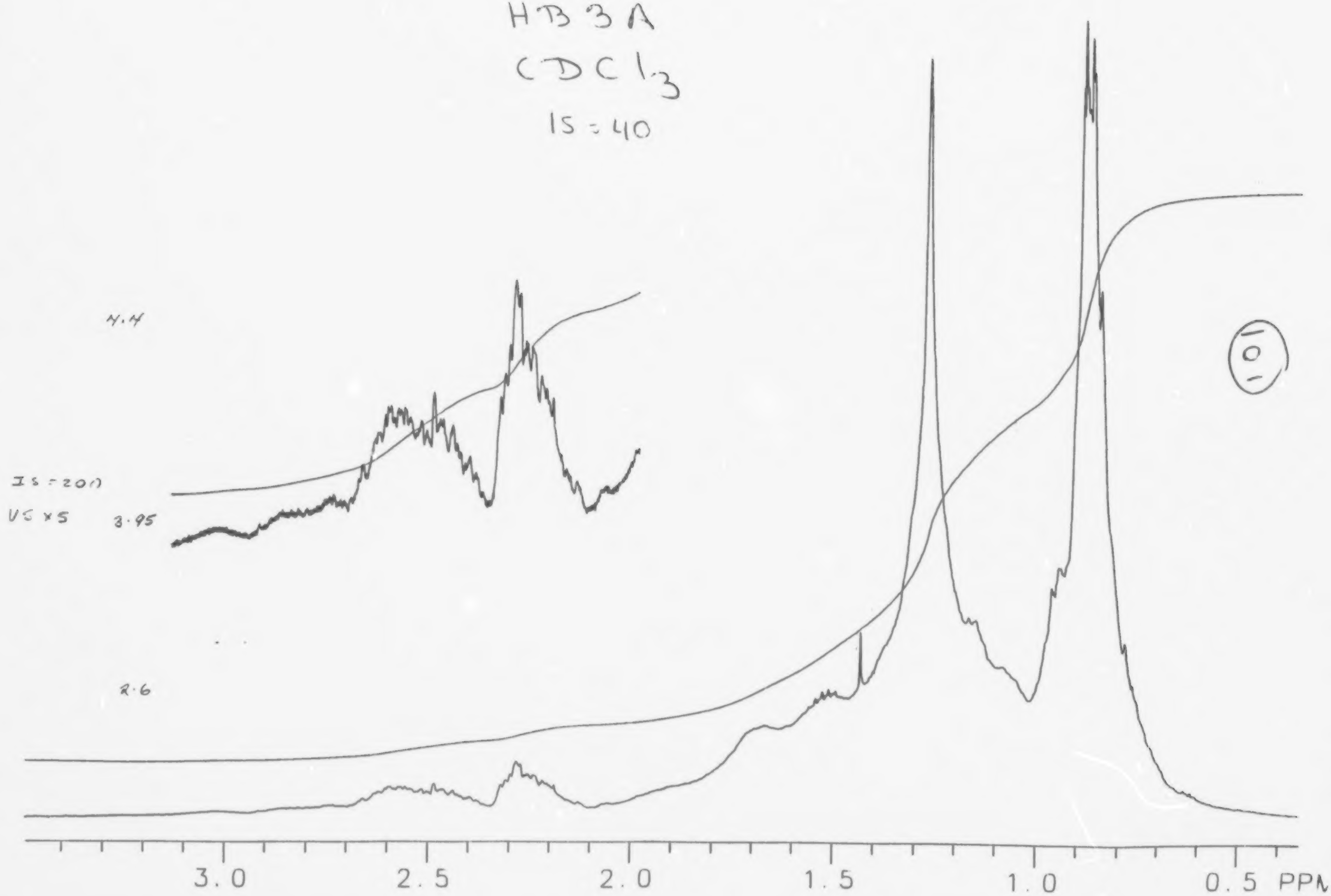


HB3A
$CDCl_3$
IS = 800

7.25 − 0.1 ↙ $CHCl_3$
= 7.15

100

IS = 40



(101)

HB 4E 1-5-86

$CDCl_3$

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   35.29
  RFL=   249.2  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01  1394.70    3.488    69.387
 02  1387.70    3.471    69.665
 03   509.32    1.274    37.889
 04   508.47    1.272    38.760
 05   504.26    1.261    68.791
 06   489.91    1.225    89.888
 07   482.78    1.207   151.310
 08   475.87    1.190    88.134
 09   358.44    0.896    41.936
 10   354.84    0.887    54.972
 11   352.31    0.881    70.374
 12   350.62    0.877    56.789
 13   349.72    0.875    57.841
 14   348.92    0.873    58.415
 15   347.69    0.870    70.624
 16   345.32    0.864    60.739
 17   343.73    0.860    56.667
 18   342.93    0.858    55.479
 19   341.05    0.853    64.012
 20   340.49    0.852    61.525
 21   334.48    0.836    38.683
```

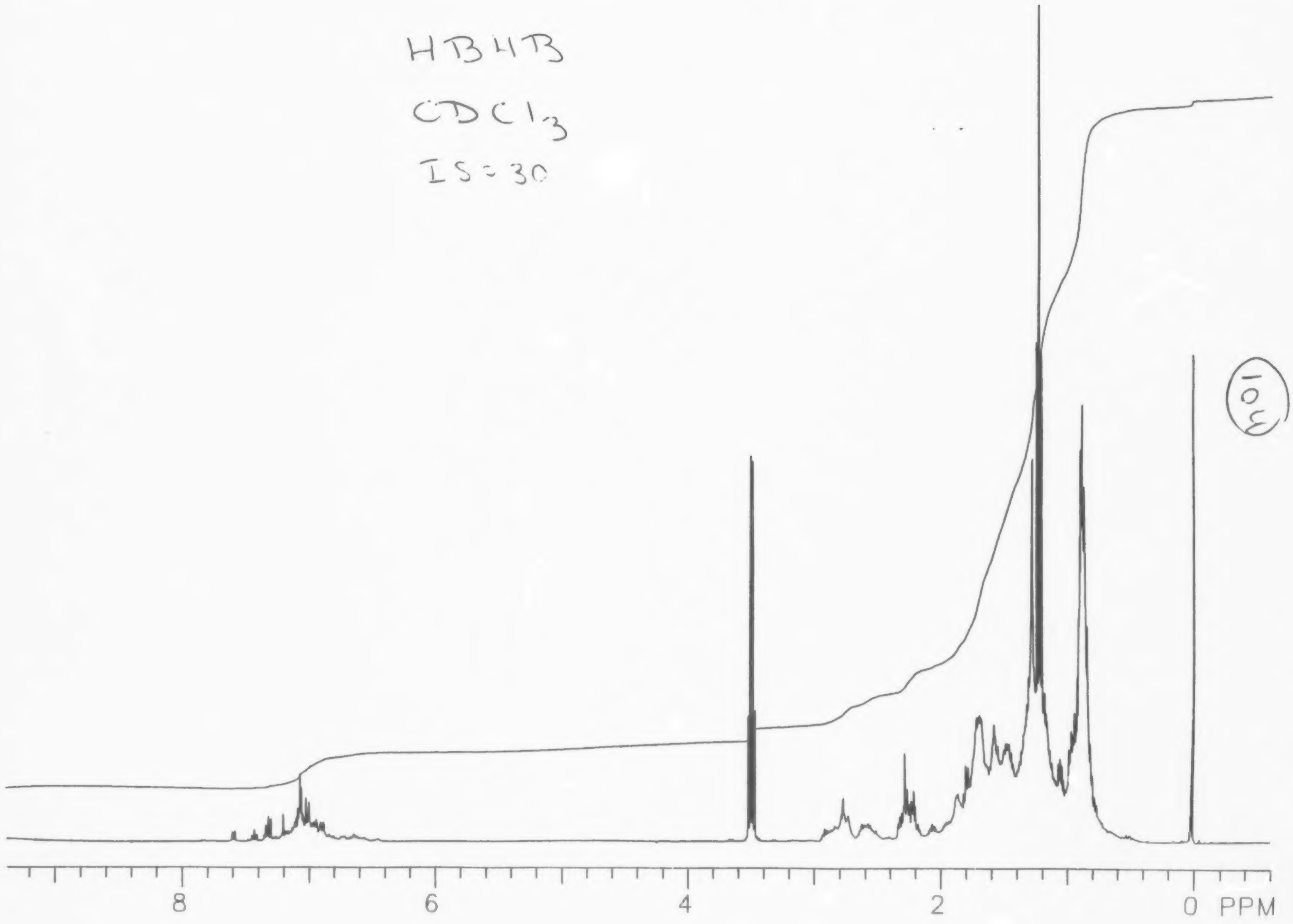
```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   20.27
  RFL=   249.2  RFP=       0

INDEX  FREQ      PPM   INTENSITY
 01  1401.79    3.506    22.886
 02  1394.70    3.488    69.709
 03  1387.70    3.471    69.984
 04  1380.64    3.453    23.896
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   20.27
  RFL=   249.2  RFP=        0

INDEX  FREQ       PPM   INTENSITY
 01  1401.79    3.506   22.886
 02  1394.70    3.488   69.709
 03  1387.78    3.471   69.984
 04  1380.64    3.453   23.896
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   63.32
  RFL=   249.2  RFP=        0

INDEX  FREQ       PPM   INTENSITY
 01    504.26   1.261   72.569
 02    489.91   1.225   94.879
 03    482.78   1.207  159.856
 04    475.87   1.190   93.016
 05    352.31   0.881   74.169
 06    347.69   0.870   82.893
 07    345.32   0.864   63.973
 08    341.05   0.853   67.433
 09    340.49   0.852   64.802
```

```
  ACQUISITION                                        PROCESSING
SFRQ   399.869         DATE  01-05-86         SE     NOT USED
TN       1.750         SOLVNT  CDCL3          LB     NOT USED
SW      4000.0         FILE    HB4B           RE     NOT USED
AT       3.752                                CD     NOT USED
NP       30016            DECOUPLING          CCD    NOT USED
FB        2200         DN         1.750       AF     NOT USED
BS          16         DO          74.5       FN        65536
SS           0         DM          NNN        MATH     F
PW         1.0         DLP          20
P1           0                                   SPECIAL
D1       1.000              FLAGS             TEMP   NOT USED
D2           0         IL          N          VTC        25.0
TO        -200         IN          N          PW90       13.0
NT          32         DP          Y
CT          32
```

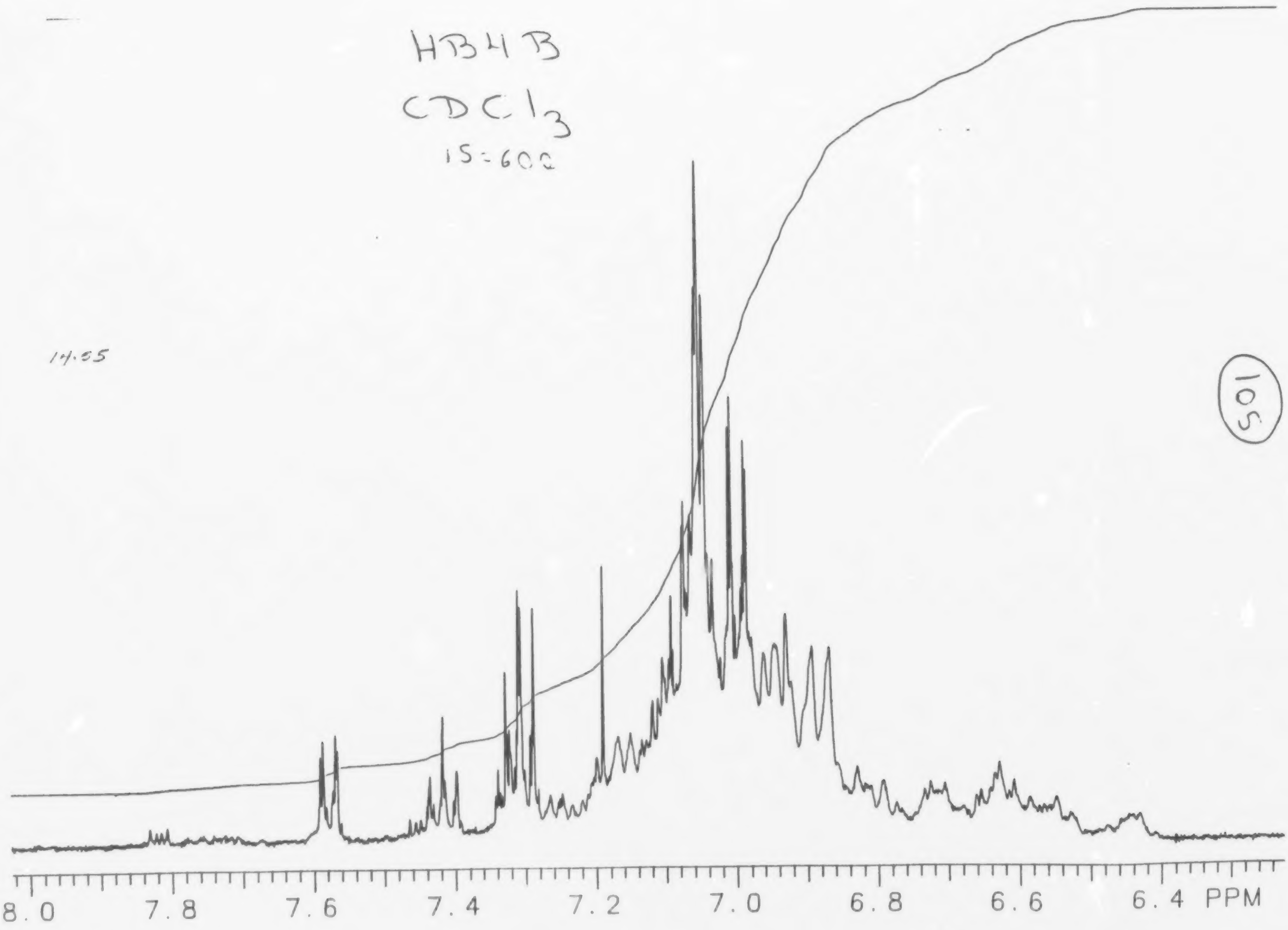
IS = 30



HBHB
$CDCl_3$
IS = 30

104

S=600



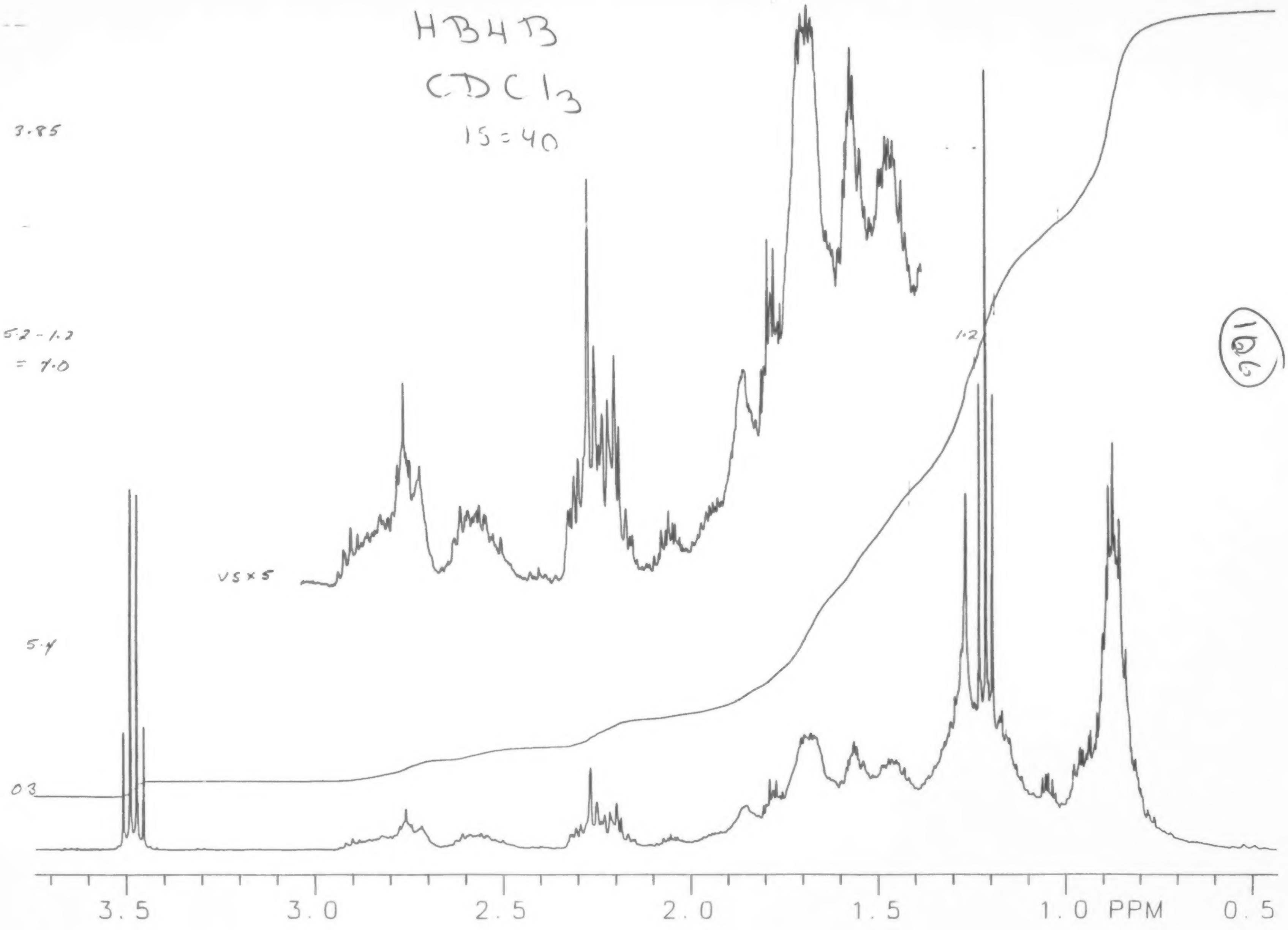
HB4B
$CDCl_3$
IS=600

14.55

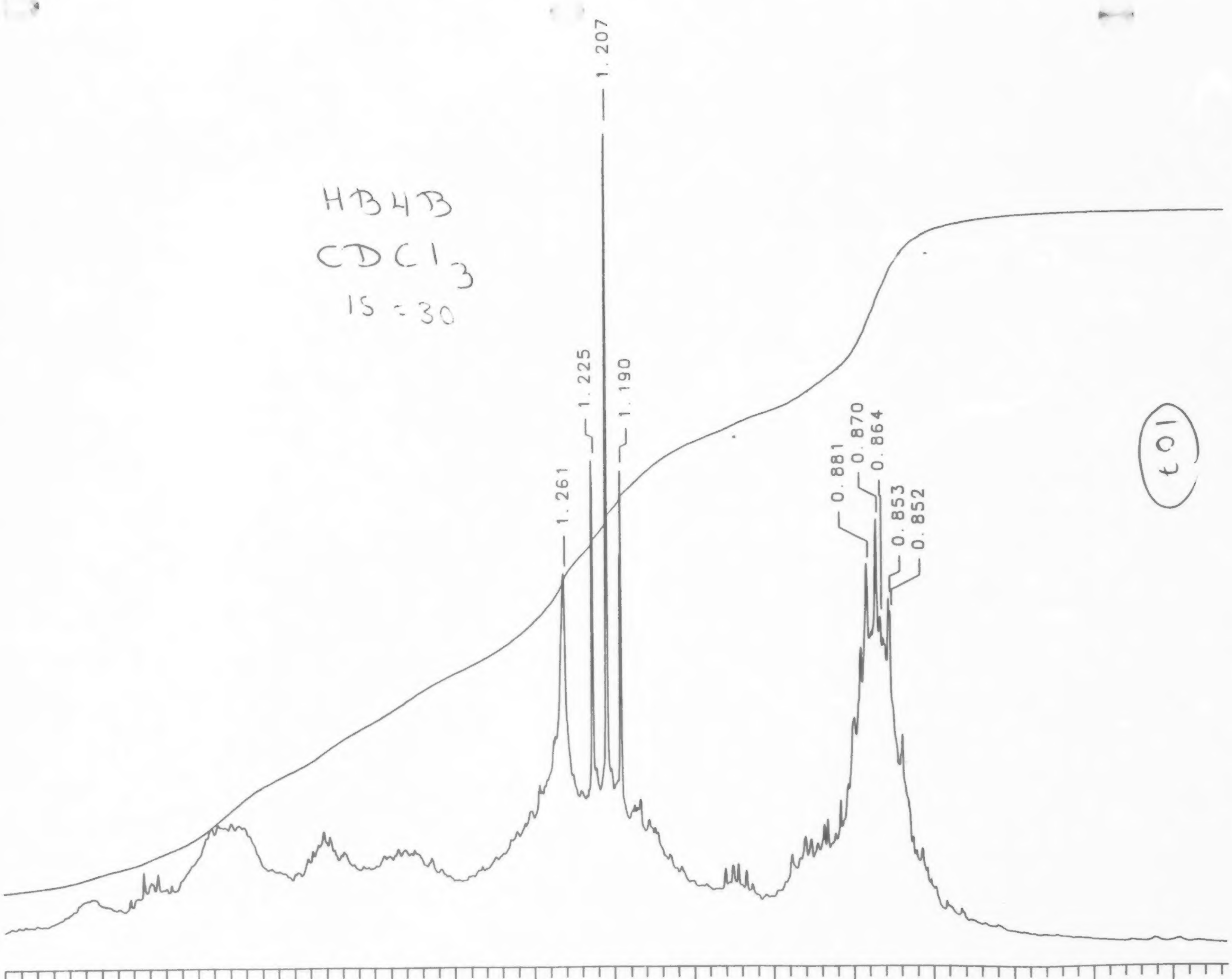
(105)

IS = 40

HB4B
CDCl3
IS = 40



IS = 30



HB4B
CDCl3
IS = 30

(107)

108

HR5B 1-5-86

$CDCl_3$

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   23.61
  RFL=   252.4  RFP=        0

INDEX  FREQ       PPM   INTENSITY
 01   504.19     1.261  138.495
 02   358.99     0.898   31.887
 03   357.34     0.894   28.906
 04   352.31     0.881   73.084
 05   350.14     0.876   49.295
 06   348.37     0.871   44.933
 07   345.38     0.864   46.559
 08   343.54     0.859   43.799
 09   341.81     0.855   44.177
 10   335.12     0.838   25.220
 11   334.27     0.836   25.787
 12   333.41     0.834   25.241
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   20.51
  RFL=   252.4  RFP=        0

INDEX  FREQ       PPM   INTENSITY
 01   907.72     2.270   41.101
 02   905.82     2.265   23.524
 03   905.27     2.264   27.941
 04   904.69     2.262   25.309
 05   899.44     2.249   41.812
 06   893.92     2.236   21.566
 07   893.37     2.234   21.541
 08   884.79     2.213   29.571
 09   872.49     2.182   36.951
 10   609.00     1.523   21.175
```

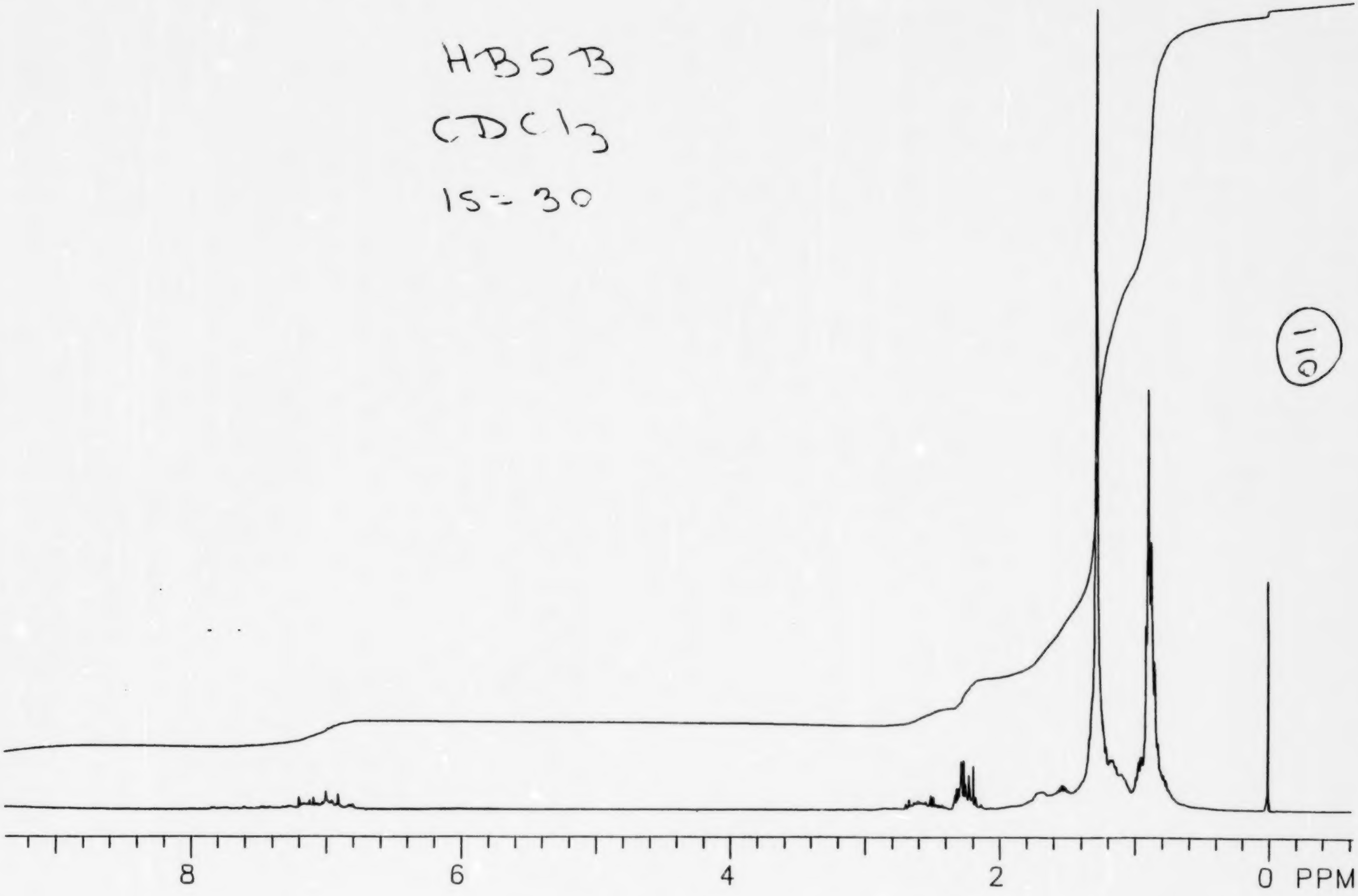
ACQUISITION PROCESSING

109

```
  ACQUISITION                                    PROCESSING
SFRQ   399.869        DATE  01-05-86        SE     NOT USED
TN       1.750        SOLVNT  CDCL3         LB     NOT USED
SW      4000.0        FILE    HB3A          RE     NOT USED
AT       3.752                              CD     NOT USED
NP       30016          DECOUPLING          CCD    NOT USED
FB        2200        DN        1.750       AF     NOT USED
BS          16        DO         74.5       FN        65536
SS           0        DM          NNN       MATH     F
PW         1.0        DLP          20
P1           0                                  SPECIAL
D1       1.000            FLAGS             TEMP   NOT USED
D2           0        IL          N         VTC        25.0
TO        -200        IN          N         PW90       13.0
NT          48        DP          Y
CT          48
```

HB5B
CDCl3
15-30

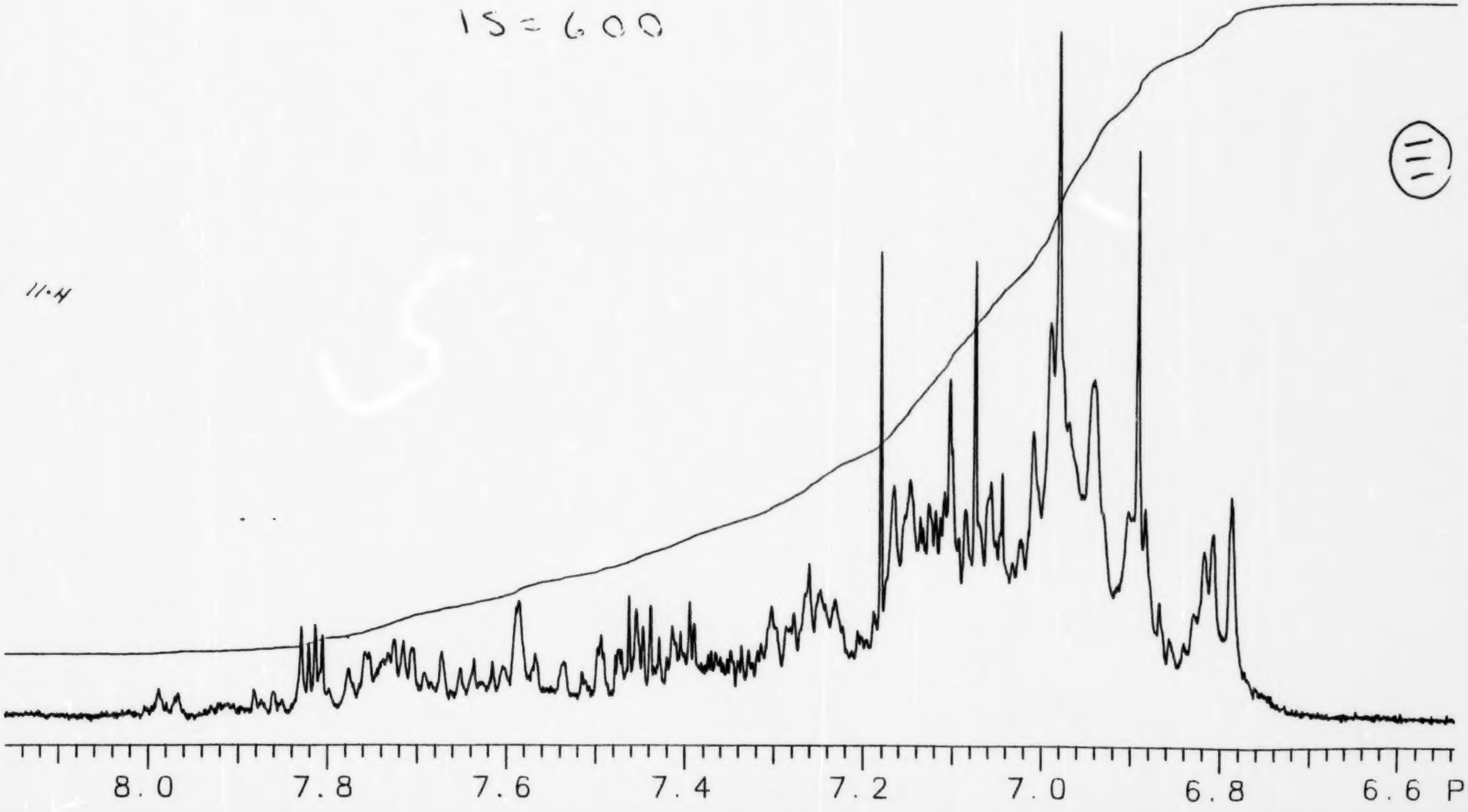
(110)



HB5B
CDCl3
IS=6.00

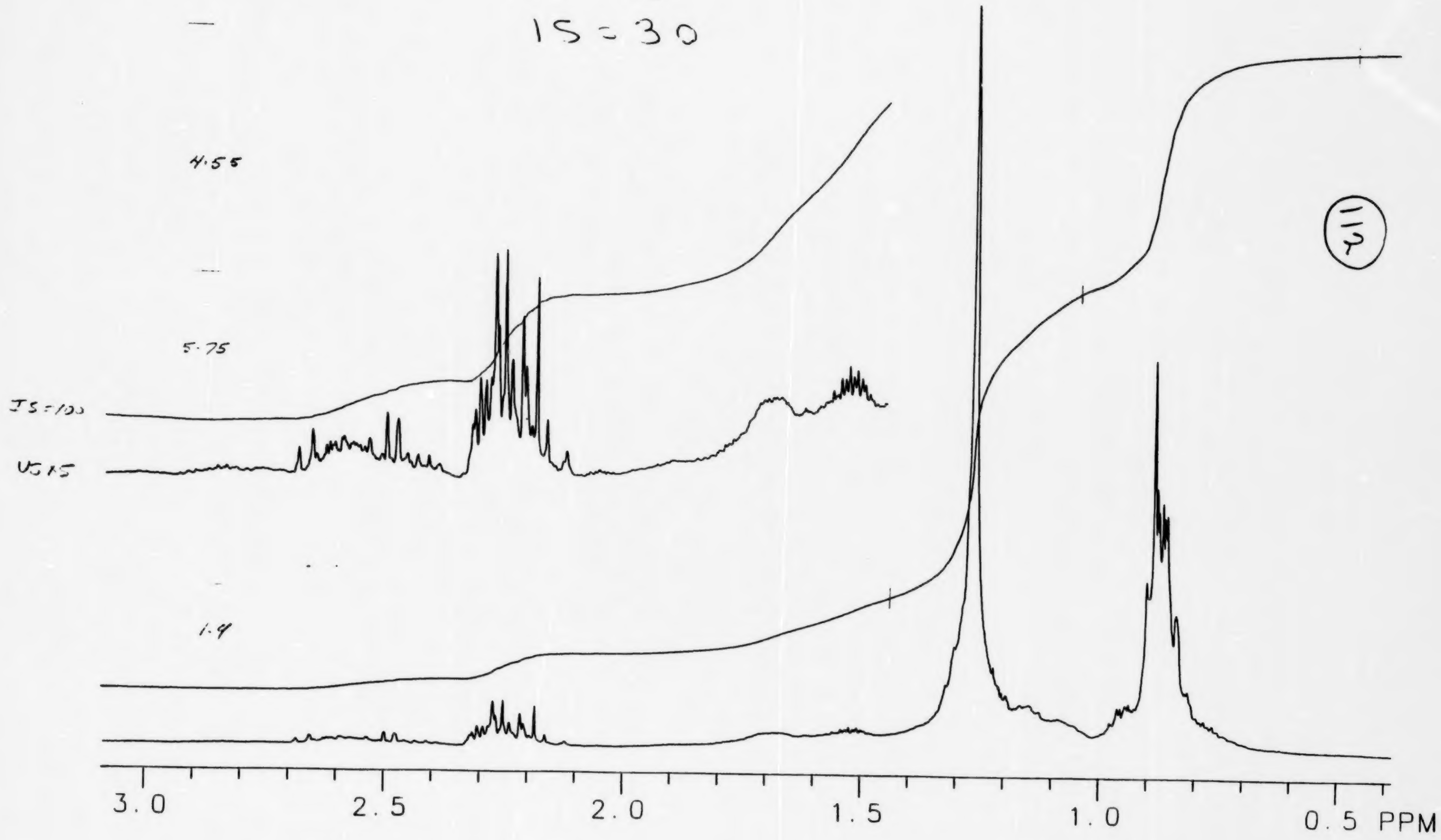
(111)

11.4



IS=30

HBSB
$CDCl_3$
IS=30



(112)

(113)

HR 6 B
$CDCl_3$

```
SPECTRAL LINES FOR TH=   68.65
 RFL=   251.6  RFP=        0

INDEX  FREQ     PPM   INTENSITY
 01   502.19   1.256  160.342
 02   486.10   1.216   83.101
 03   478.96   1.198  107.424
 04   472.06   1.181   71.020
 05   351.67   0.879  137.093
 06   350.26   0.876  129.722
 07   347.88   0.870  125.919
 08   344.76   0.862  127.218
 09   335.07   0.838   83.322
```

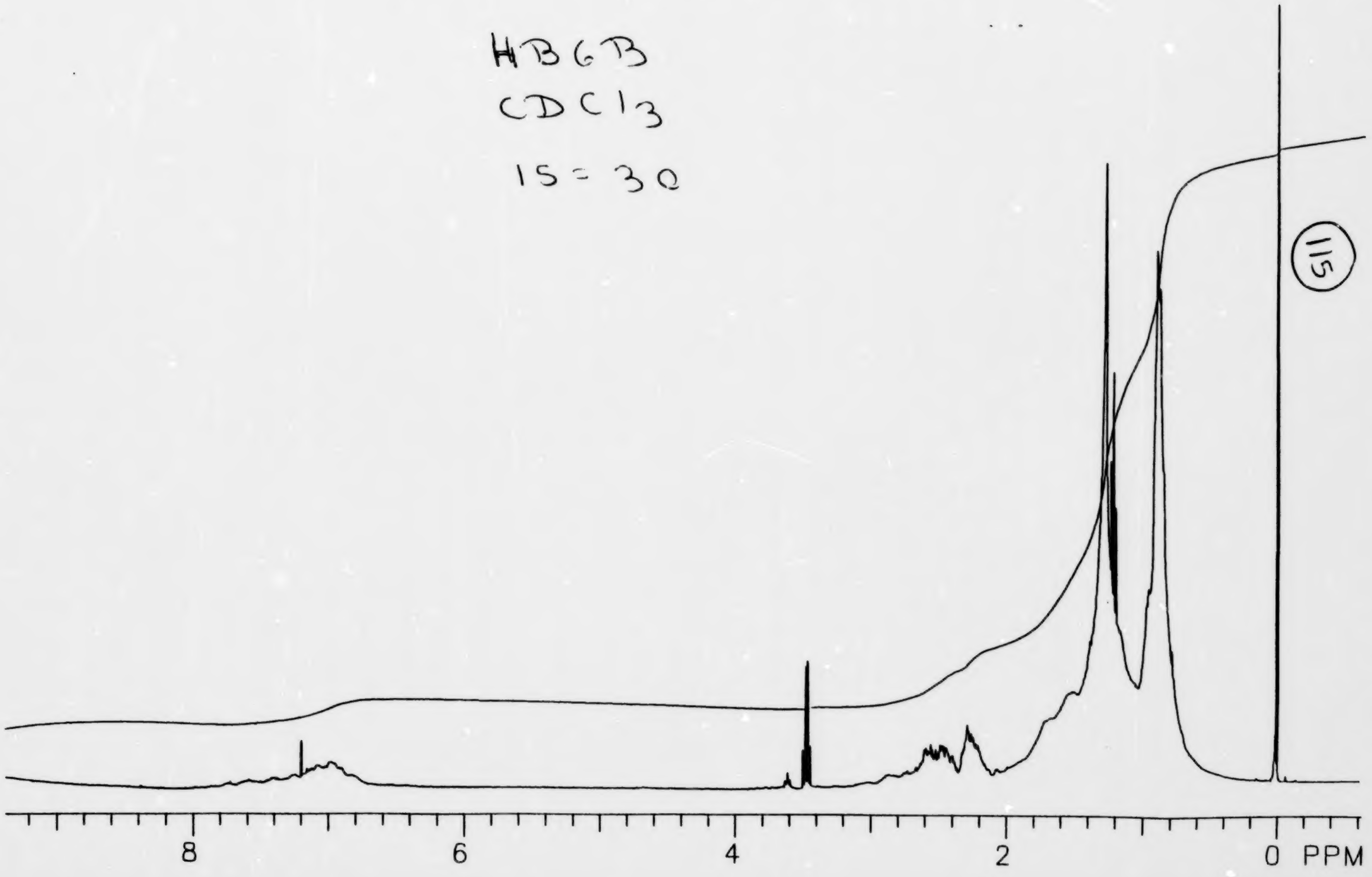
```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=    6.24
 RFL=   251.6  RFP=        0

INDEX  FREQ     PPM   INTENSITY
 01  1446.06   3.616    9.289
 02  1445.24   3.614    7.692
 03  1440.92   3.603    7.018
 04  1439.40   3.600   16.806
 05  1433.39   3.585    6.379
 06  1433.06   3.584    7.659
 07  1432.69   3.583    8.574
 08  1393.67   3.485   43.908
 09  1392.53   3.482    6.565
 10  1391.89   3.481    6.377
 11  1391.25   3.479    7.148
 12  1390.70   3.478    6.635
 13  1390.33   3.477    6.706
 14  1389.47   3.475    7.129
 15  1388.89   3.473    7.123
 16  1386.76   3.468  137.590
 17  1385.27   3.464   10.188
 18  1384.17   3.462    8.591
 19  1383.44   3.460    7.937
 20  1383.10   3.459    8.052
 21  1382.42   3.457    8.023
 22  1381.91   3.456    7.973
 23  1379.65   3.450  136.550
 24  1372.72   3.433   44.115
```

114

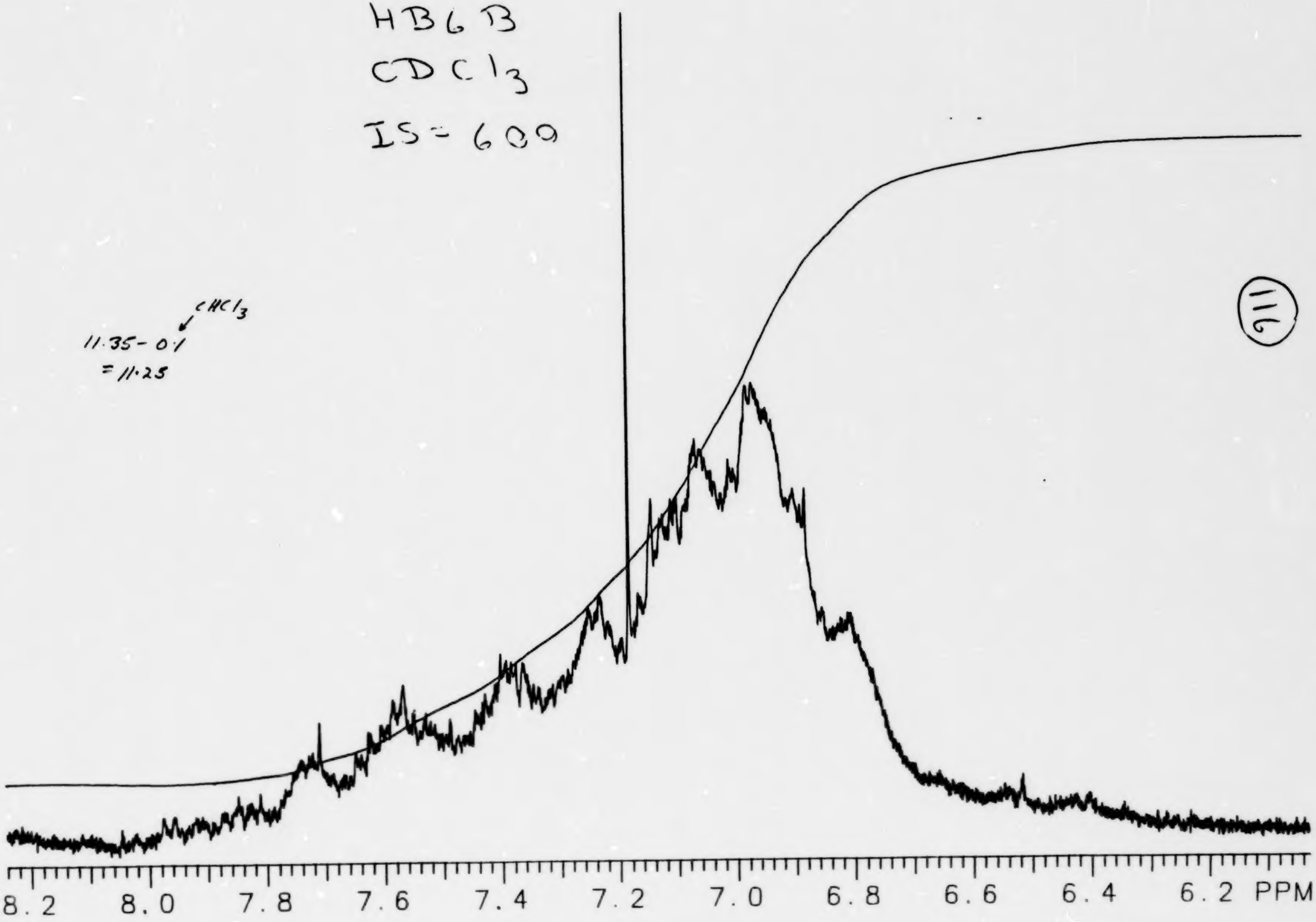
```
  ACQUISITION                                     PROCESSING
SFRQ   399.869         DATE  01-05-86         SE     NOT USED
TN       1.750         SOLVNT  CDCL3          LB     NOT USED
SW      4000.0         FILE    HB6B           RE     NOT USED
AT       3.752                                CD     NOT USED
NP       30016           DECOUPLING           CCD    NOT USED
FB        2200         DN        1.750        AF     NOT USED
BS          16         DO         74.5        FN        65536
SS           0         DM          NNN        MATH     F
PW         1.0         DLP          20
P1           0                                   SPECIAL
D1       1.000              FLAGS             TEMP   NOT USED
D2           0         IL          N          VTC        25.0
TO        -200         IN          N          PW90       13.0
NT          48         DP          Y
CT          48
```

IS-30

HBGB
$CDCl_3$
IS = 30



IS = 600

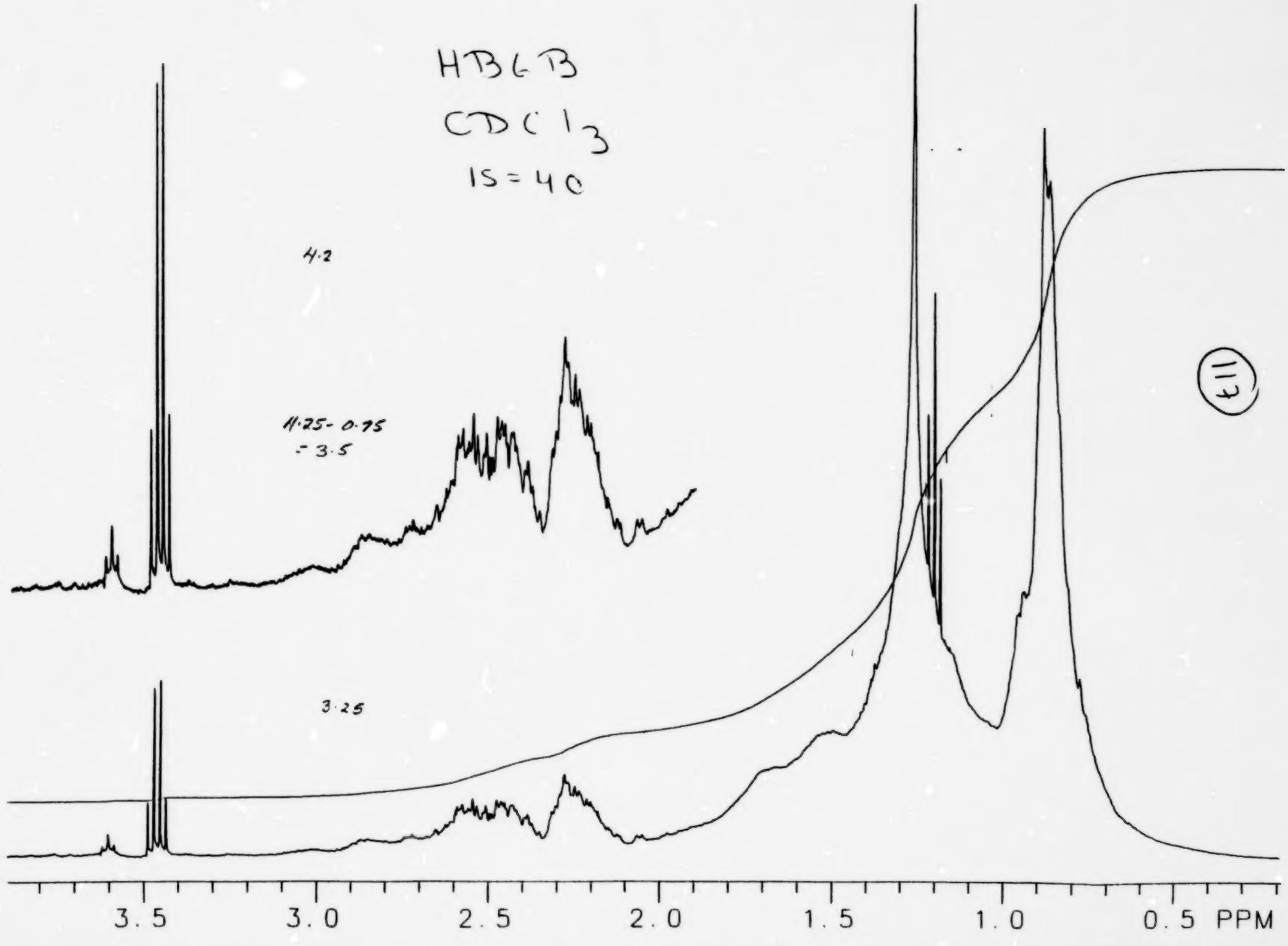


HB6B
CDCl$_3$
IS = 600

CHCl$_3$
11.35 − 0.1
= 11.25

(116)

IS = 40



HB6B
$CDCl_3$
IS = 40

4.2

11.25 - 0.75
= 3.5

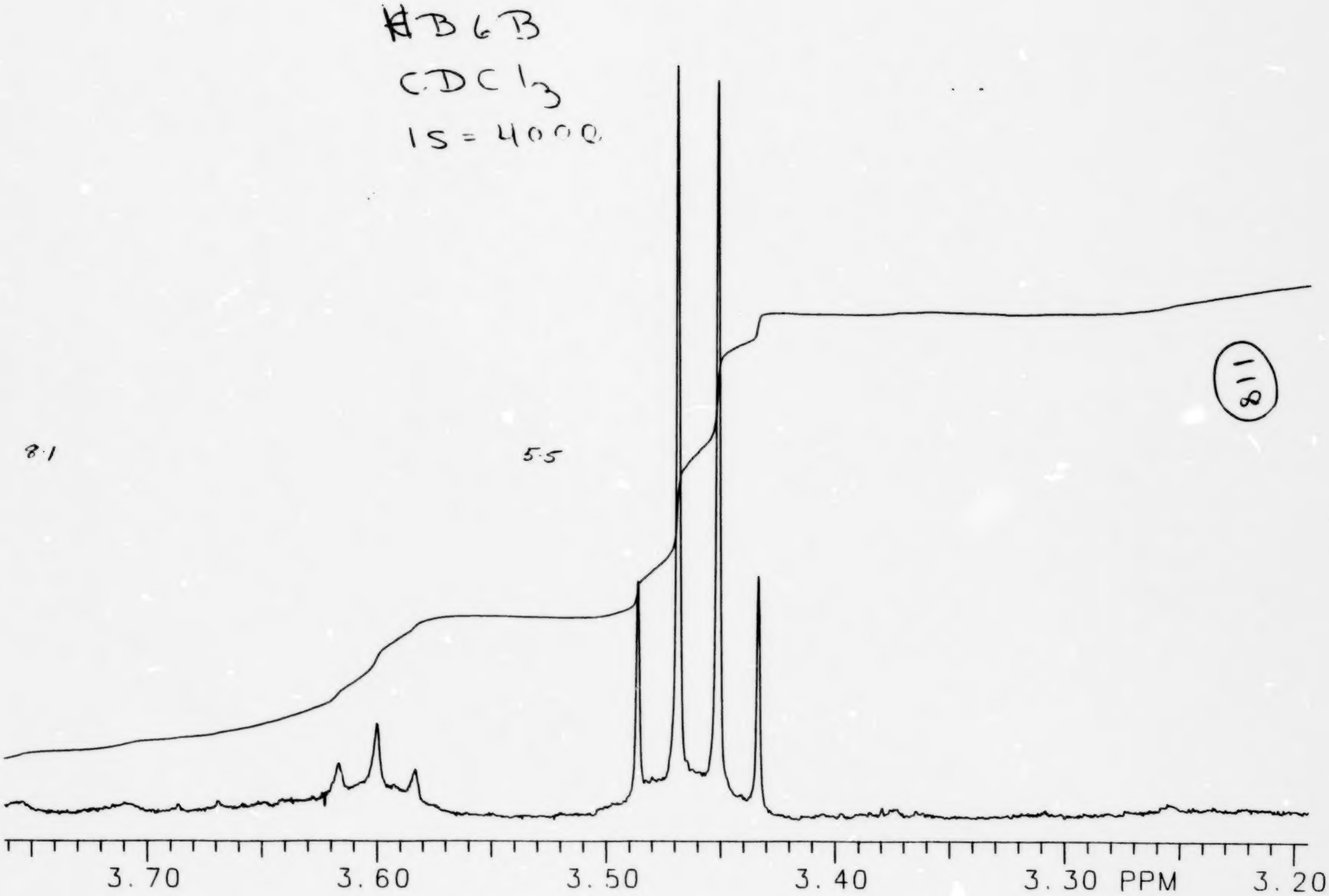
1.5 × 3

3.25

(117)

C:- 4/000

(118)


#B6B
CDCl$_3$
IS = 4000

(119)

HB 7B 1-5-86

CDCl3

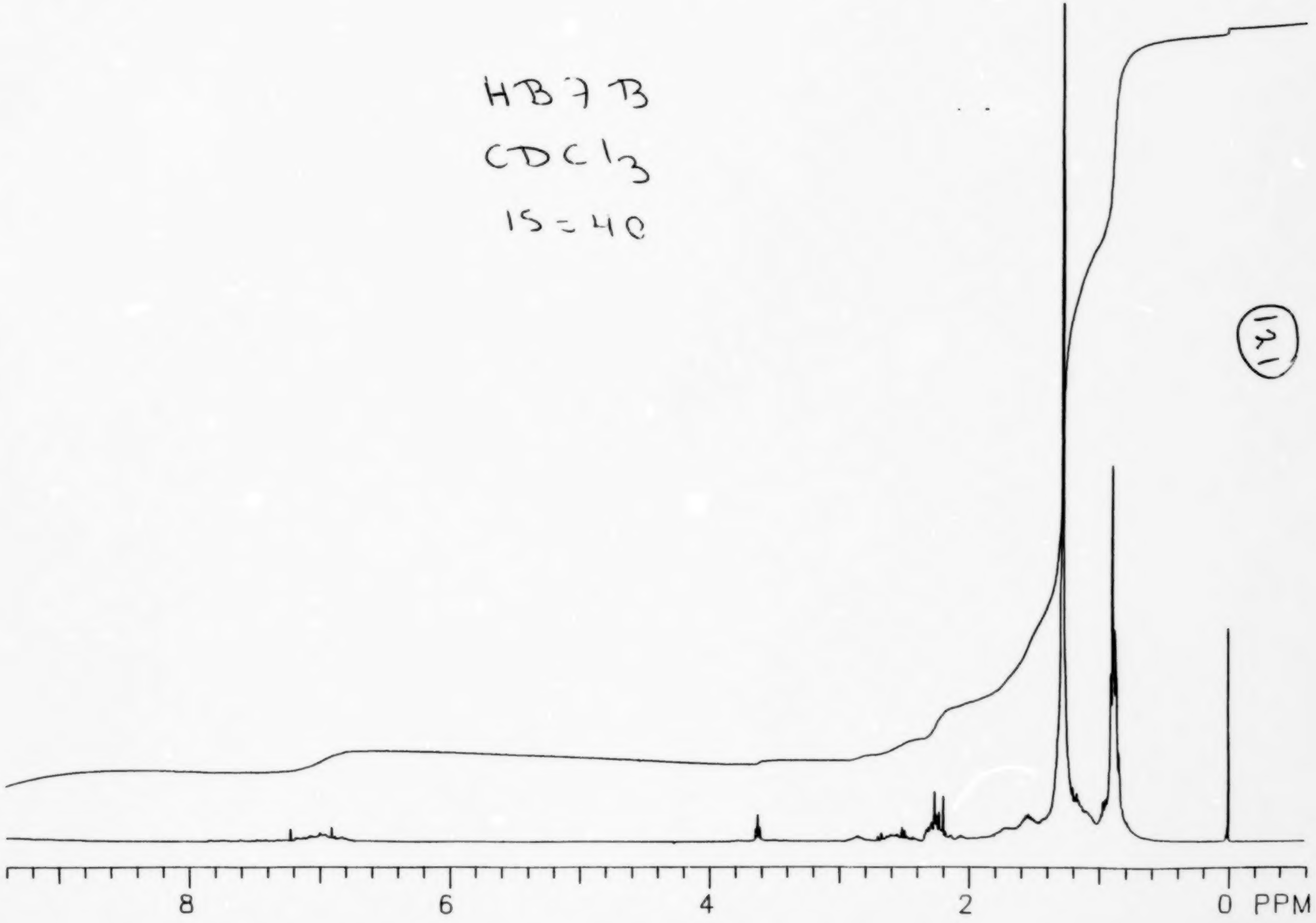
```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   27.16
 RFL=   240.6  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01   512.74    1.282   31.197
 02   503.68    1.260  154.616
 03   358.93    0.898   30.945
 04   352.21    0.881   69.340
 05   350.01    0.875   35.190
 06   348.16    0.871   33.333
 07   345.10    0.863   38.889
 08   343.37    0.859   29.454
 09   341.59    0.854   30.349
```

```
XL-400 1H OBSERVE
SPECTRAL LINES FOR TH=   14.38
 RFL=   240.6  RFP=        0

INDEX  FREQ      PPM   INTENSITY
 01  1450.82    3.628   14.613
 02  1444.26    3.612   30.123
 03  1437.52    3.595   16.581
 04   999.88    2.501   14.542
 05   912.23    2.281   15.167
 06   911.53    2.280   15.431
 07   910.21    2.276   17.885
 08   909.70    2.275   18.943
 09   908.94    2.273   19.875
 10   900.27    2.251   53.221
 11   894.93    2.238   28.087
 12   894.41    2.237   26.967
 13   891.97    2.231   16.059
 14   891.53    2.230   15.864
 15   891.17    2.229   15.857
 16   885.40    2.214   30.797
 17   873.32    2.184   40.139
```

```
   ACQUISITION                                       PROCESSING
SFRQ   399.869       DATE  01-05-86            SE     NOT USED
TN       1.750       SOLVNT  CDCL3             LB     NOT USED
SW      4000.0       FILE    HB1B              RE     NOT USED
AT       3.752                                 CD     NOT USED
NP       30016          DECOUPLING             CCD    NOT USED
FB        2200       DN        1.750           AF     NOT USED
BS          16       DO         74.5           FN        65536
SS           0       DM          NNN           MATH      F
PW         1.0       DLP           20
P1           0                                    SPECIAL
D1       1.000             FLAGS               TEMP  NOT USED
D2           0       IL          N             VTC        25.0
TO        -200       IN          N             PW90       13.0
NT          48       DP          Y
CT          48
```

S = 40

(121)



HB7B
$CDCl_3$
IS = 40

HB7B

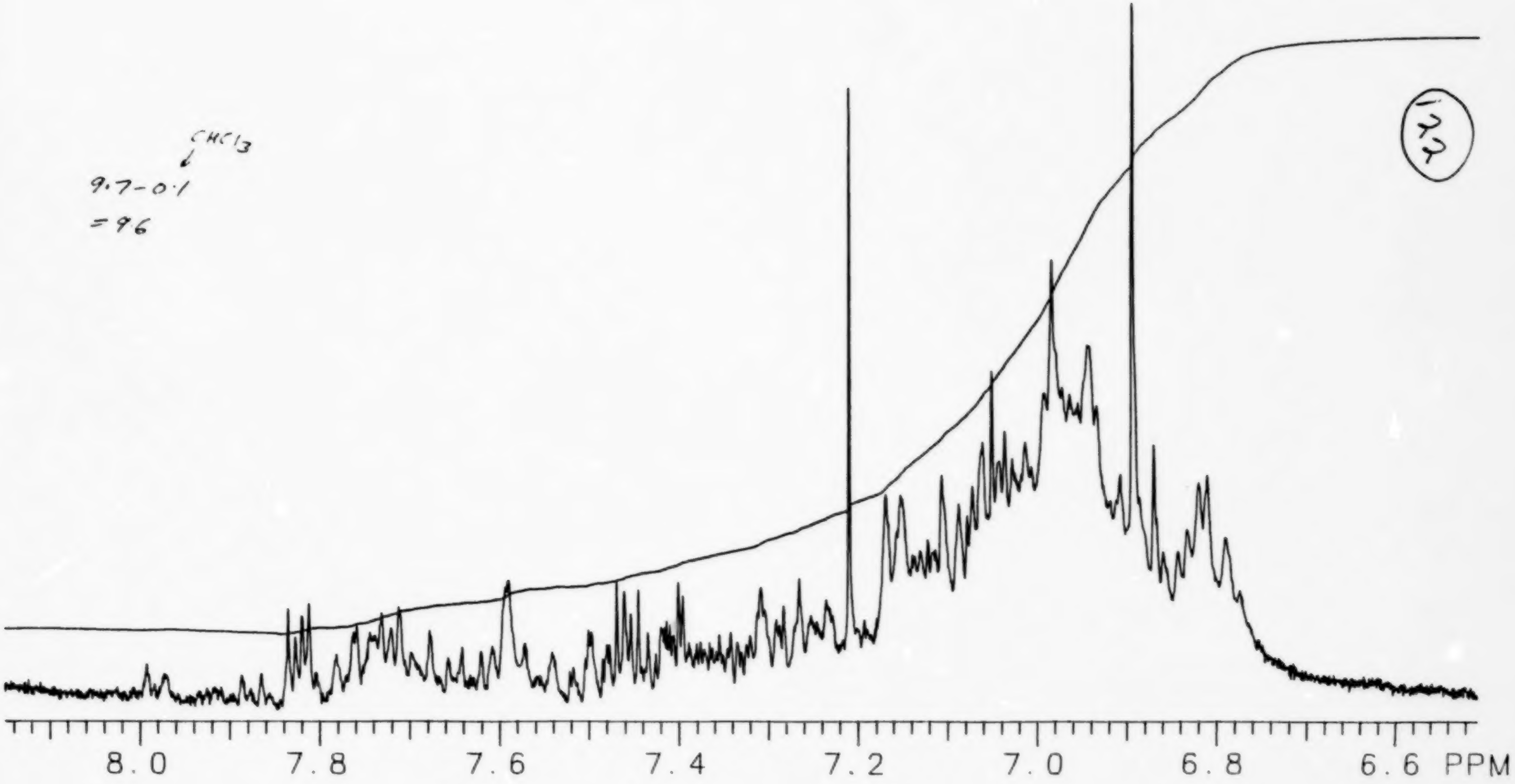
$CDCl_3$

IS = 800

$CHCl_3$

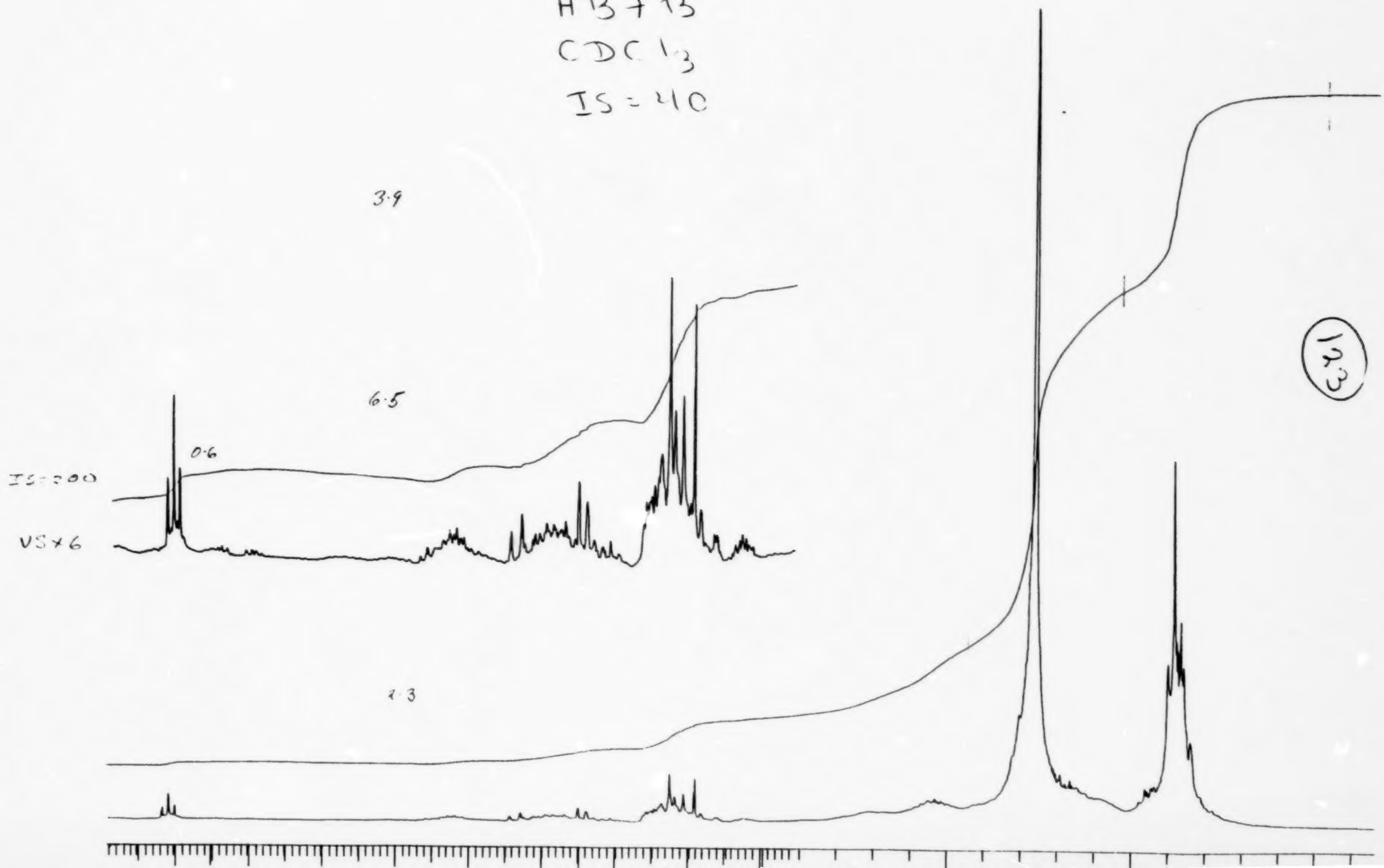
9.7-0.1

=9.6



IS=40

HB7B
$CDCl_3$
IS=40



(123)

(124)

API ^{13}C SUNCOR COKER CDCl$_3$

```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   20.00
 RFL=  7906.1  RFP=  7743.0

INDEX  FREQ      PPM   INTENSITY
 01   3219.2   32.013   74.209
 02   2996.1   29.794  129.160
 03   2992.0   29.754   88.458
 04   2962.0   29.455   78.249
 05   2288.8   22.761   76.037
 06   2280.3   22.676   27.207
 07   2276.8   22.641   24.172
 08   1421.1   14.132   74.045
```

```
  ACQUISITION                                   PROCESSING
SFRQ   100.559        DATE  18-04-86        SE         0.318
TN      13.750        SOLVNT  CDCL3         LB         1.000
SW     20000.0        FILE    C             RE      NOT USED
AT       0.819                              CD      NOT USED
NP       32768           DECOUPLING         CCD     NOT USED
FB       11000        DN         1.750      AF      NOT USED
BS         100        DO          96.4      FN         65536
SS           0        DM         YYY        MATH     F
PW        13.5        DMM        S
P1           0        DMF         7600         SPECIAL
D1       1.300        DHP        Y          TEMP  NOT USED
D2           0        DLP           20      VTC         25.0
TC           0                              PAD        0.500
NT         200             FLAGS            PW90        25.0
CT         200        IL         N
                      IN         Y
                      DP         N
                      HS         NN
```

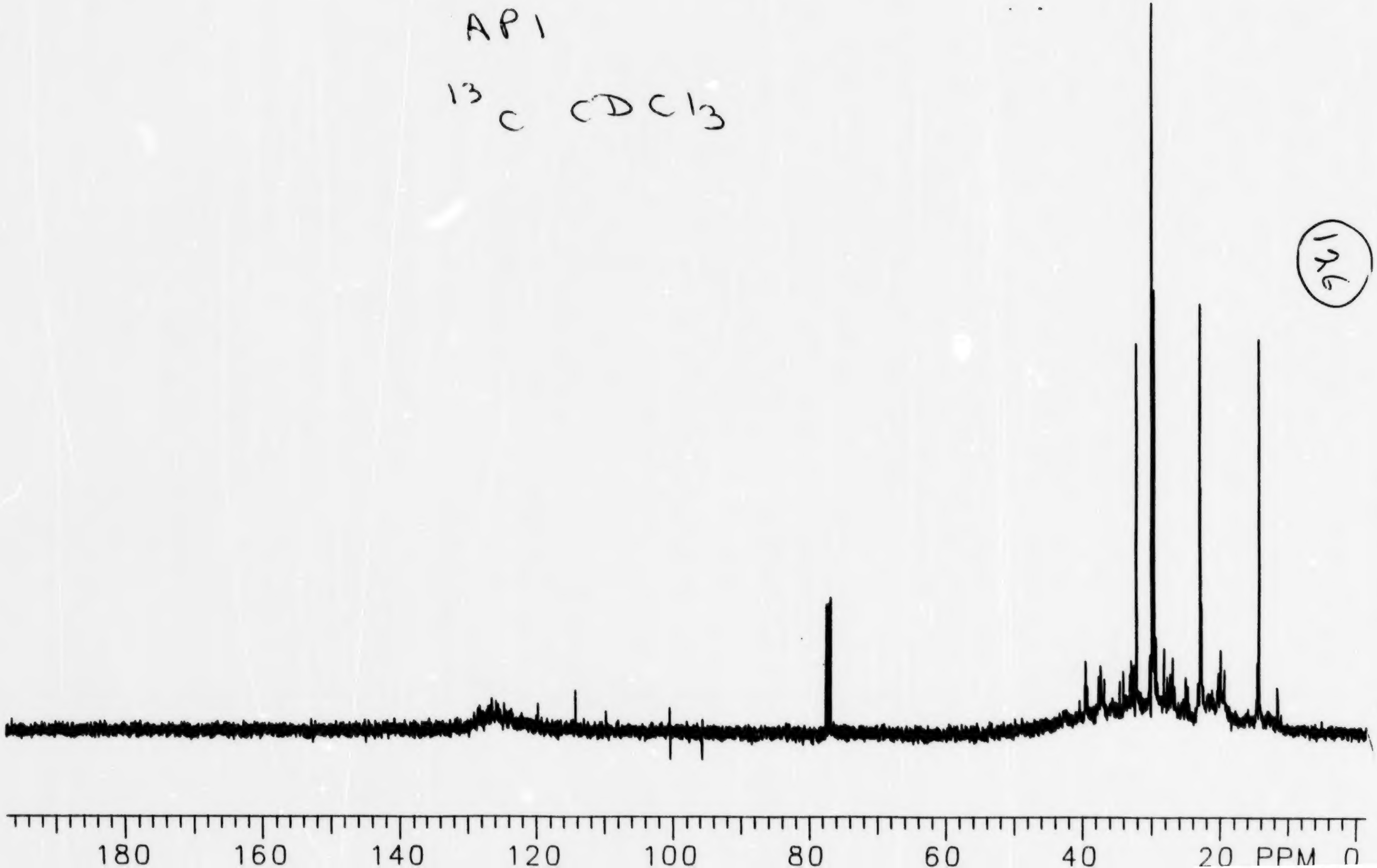
125

```
                                                          PROCESSING
  ACQUISITION
SFRQ    100.559        DATE  10-04-86            SE          0.310
TN       13.750        SOLVNT  CDCL3             LB          1.000
SW      20000.0        FILE    APT               RE       NOT USED
AT        0.819                                  CD       NOT USED
NP        32768          DECOUPLING              CCD      NOT USED
FB        11000        DN          1.750         AF       NOT USED
BS          100        DO           96.4         FN          65536
SS            0        DM          YNY           MATH     F
PW         13.5        DMM         S
P1         27.0        DMF          7600            SPECIAL
D1        1.000        DHP         Y             TEMP     NOT USED
D2      7.00E-3        DLP            20         VTC          25.0
TO            0                                  PAD         0.500
NT          200             FLAGS                PW90         25.0
CT          200        IL          N
D3      1.01E-3        IN          Y
                       DP          N
                       HS          NN
```

HP1
SU R
CO R

AP1

^{13}C $CDCl_3$



(126)

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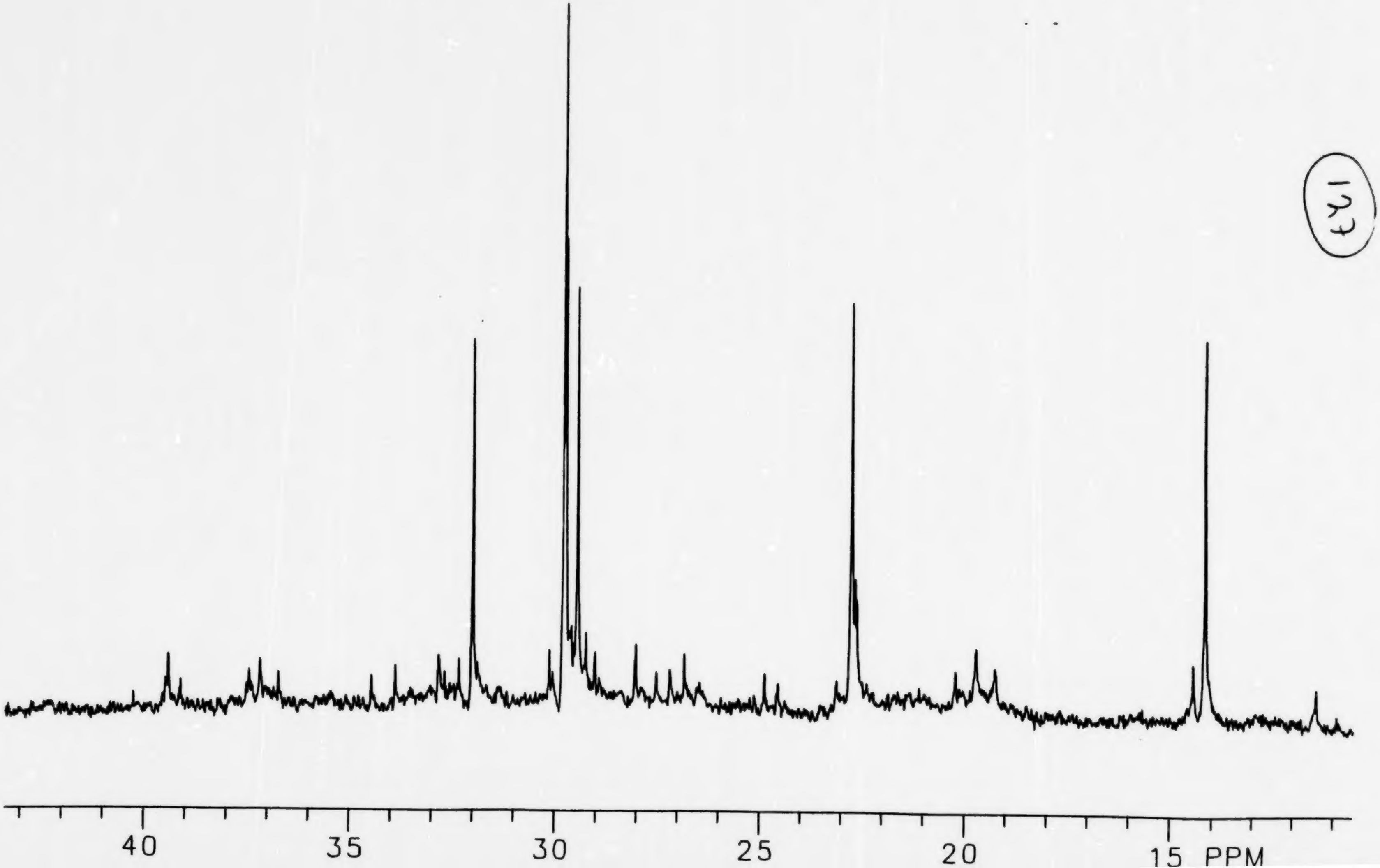
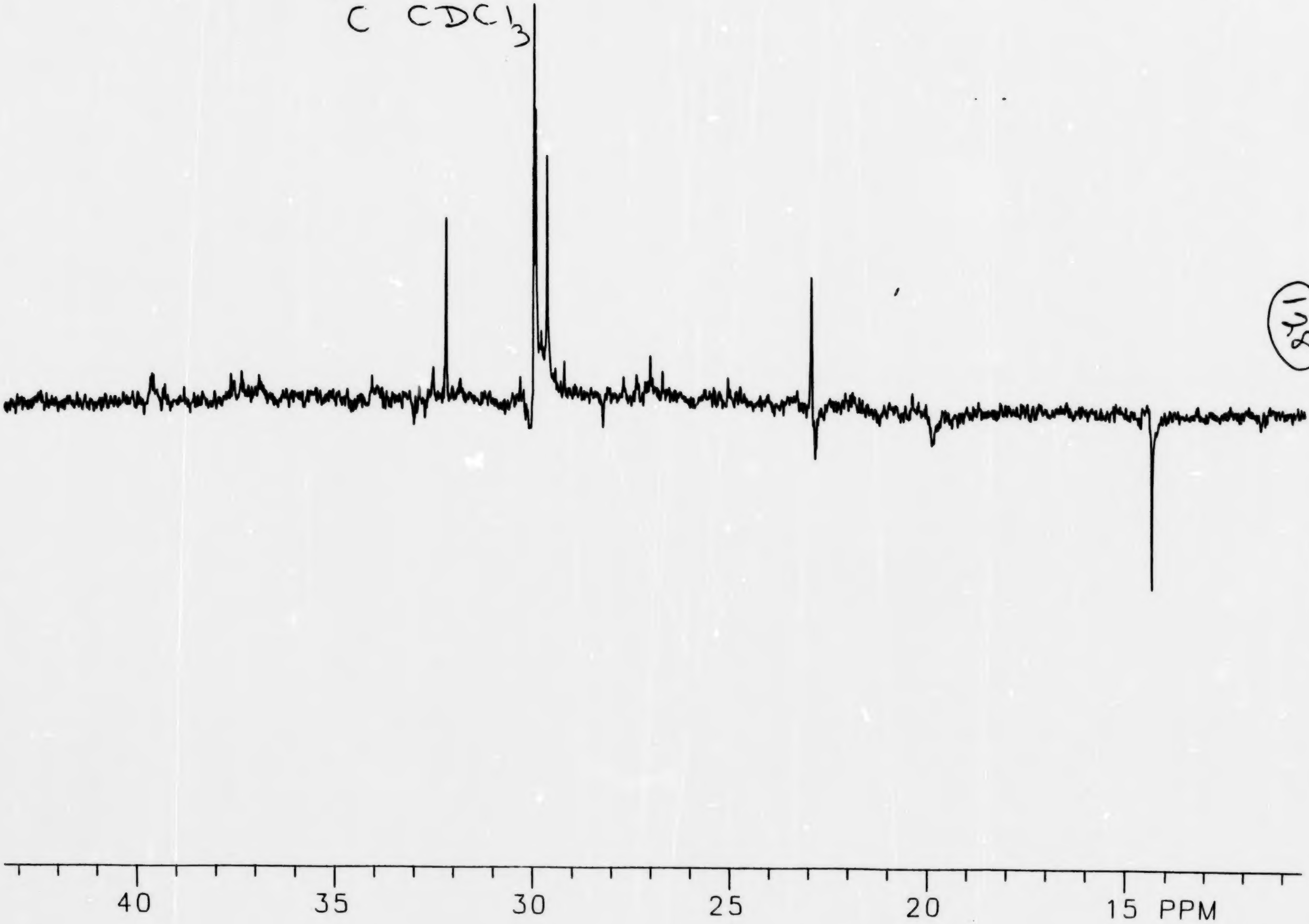
AP I

^{13}C CDCl$_3$





AP 1

^{13}C $CDCl_3$

AP4 WYODAK ^{13}C

$CDCl_3$

```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   16.62
 RFL=  7902.5  RFP=  7743.0

INDEX  FREQ      PPM   INTENSITY
 01  13780.7  137.041   19.008
 02  13758.5  136.821   17.870
 03  13040.3  129.678  109.986
 04  13009.8  129.375   18.361
 05  12993.3  129.210   22.431
 06  12982.4  129.102   75.244
 07  12975.7  129.036   23.288
 08  12973.9  129.018   40.781
 09  12971.6  128.995   54.976
 10  12962.6  128.906   17.835
 11  12955.6  128.836   34.224
 12  12948.0  128.760   25.523
 13  12942.5  128.706   66.577
 14  12896.3  128.246   20.038
 15  12892.1  128.204   19.693
 16  12889.8  128.181   20.242
 17  12876.9  128.053   21.247
 18  12796.9  127.258   17.916
 19  12791.2  127.201   48.595
 20  12785.5  127.145   58.616
 21  12770.8  126.998   29.848
 22  12763.0  126.921   27.186
 23  12752.9  126.820   24.500
 24  12749.1  126.783   19.402
 25  12703.0  126.324   17.286
 26  12699.3  126.287   31.419
 27  12696.4  126.259   68.470
 28  12691.5  126.210   21.606
 29  12678.1  126.076   21.981
 30  12670.6  126.002   18.243
 31  12668.8  125.983   21.746
 32  12666.0  125.956   24.353
 33  12644.3  125.740   19.811
 34  12640.7  125.705   18.269
 35  12608.7  125.387  138.400
 36  12578.6  125.086   36.893
 37  12575.4  125.055   25.372
 38  12503.2  124.337   21.703
 39  12384.9  123.160   81.843
 40  11953.2  118.868  135.293
 41  11594.4  115.300   18.122
 42  11585.3  115.209   20.935
 43  11563.1  114.988   18.275
```

```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   42.60
 RFL=  7902.5  RFP=  7743.0

INDEX  FREQ       PPM    INTENSITY
 01    3945.7   39.238   62.593
 02    3568.5   35.487   51.155
 03    3443.5   34.244   78.040
 04    3370.6   33.518   87.752
 05    3366.0   33.473   81.716
 06    3322.8   33.043   61.613
 07    3217.1   31.992  105.954
 08    3037.4   30.205   53.326
 09    2994.3   29.777  119.717
 10    2990.2   29.736   84.717
 11    2960.1   29.437  107.586
 12    2956.7   29.403  155.157
 13    2946.8   29.304   43.207
 14    2916.7   29.005   47.129
 15    2770.4   27.550   85.716
 16    2708.7   26.936   73.855
 17    2697.1   26.821  141.494
 18    2693.7   26.787   73.141
 19    2691.9   26.769  108.143
 20    2687.9   26.730   50.597
 21    2685.3   26.704   56.787
 22    2679.6   26.647   53.439
 23    2665.9   26.511  144.979
 24    2660.0   26.452   50.426
 25    2353.8   23.407  117.026
 26    2337.9   23.249   80.853
 27    2313.6   23.008   54.303
 28    2290.2   22.775   55.362
 29    2287.5   22.748   83.961
 30    2224.8   22.124   54.602
 31    2106.1   20.944   43.116
 32    1449.3   14.412   66.773
 33    1423.6   14.156   48.616
 34    1420.2   14.123   85.277
```

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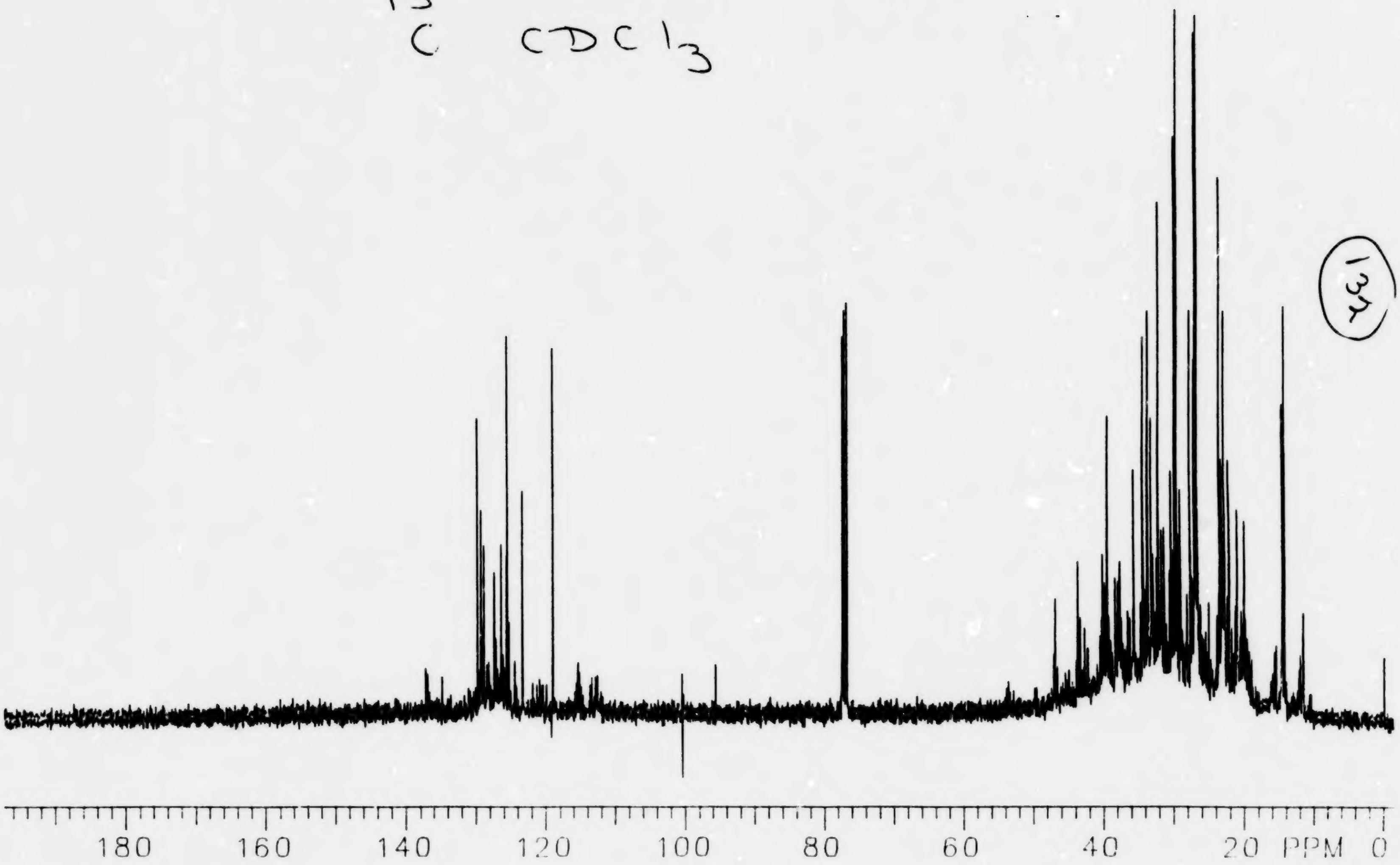
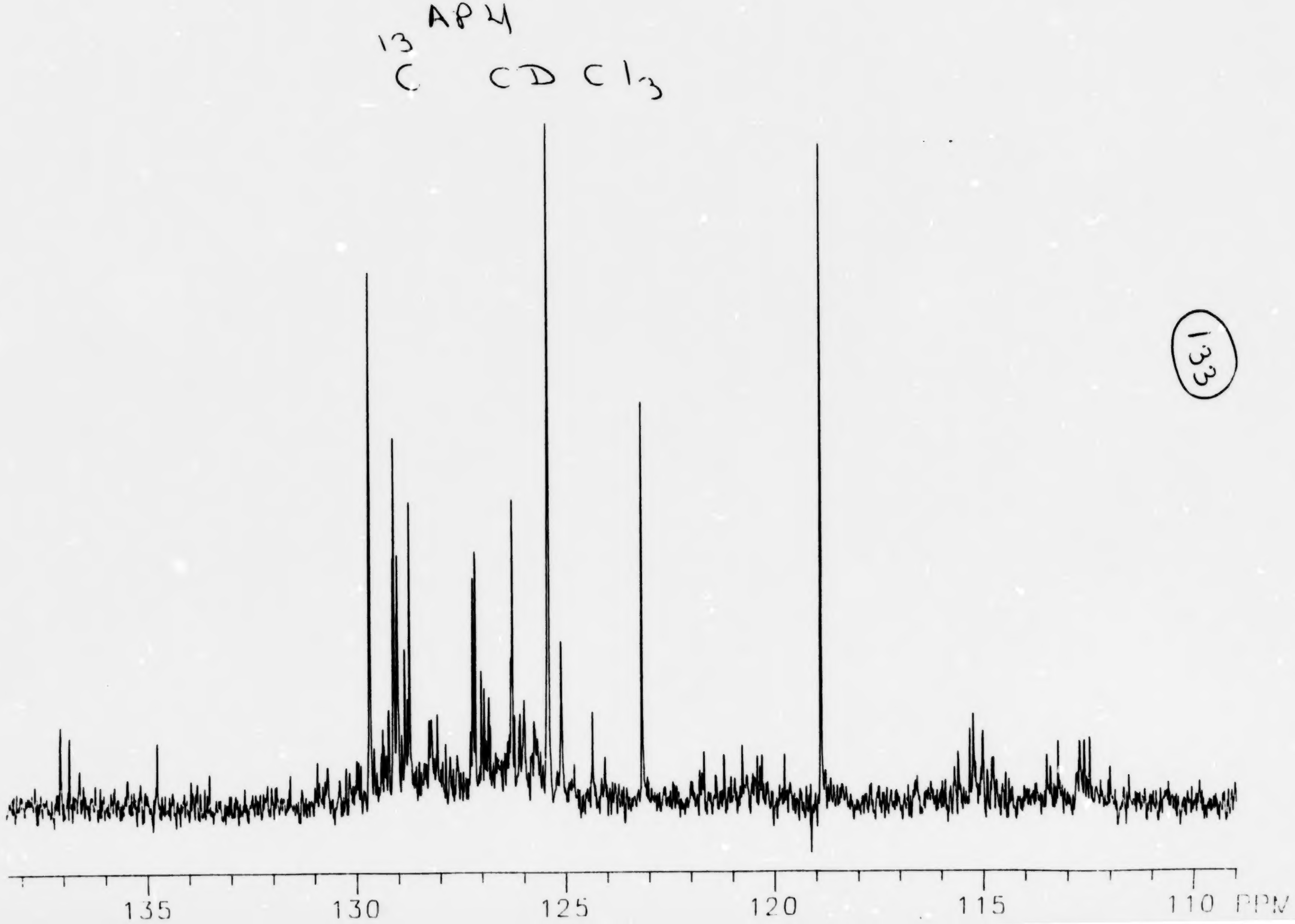
```
  ACQUISITION                                     PROCESSING
SFRQ   100.559        DATE  28-04-86           SE        0.318
TN      13.750        SOLVNT  CDCL3            LB        1.000
SW     20000.0        FILE    C                RE     NOT USED
AT       0.819                                 CD     NOT USED
NP       32768           DECOUPLING            CCD    NOT USED
FB       11000        DN         1.750         AF     NOT USED
BS         100        DO          74.5         FN        65536
SS           0        DM        YYY            MATH     F
PW        13.5        DMM       S
P1           0        DMF         7600             SPECIAL
D1       1.000        DHP       Y              TEMP   NOT USED
D2           0        DLP           20         VTC        25.0
TO           0                                 PAD       0.500
NT        2000             FLAGS               PW90       25.0
CT        1163        IL        N
                      IN        Y
                      DP        N
                      HS        NN
```

AP4
^{13}C $CDCl_3$

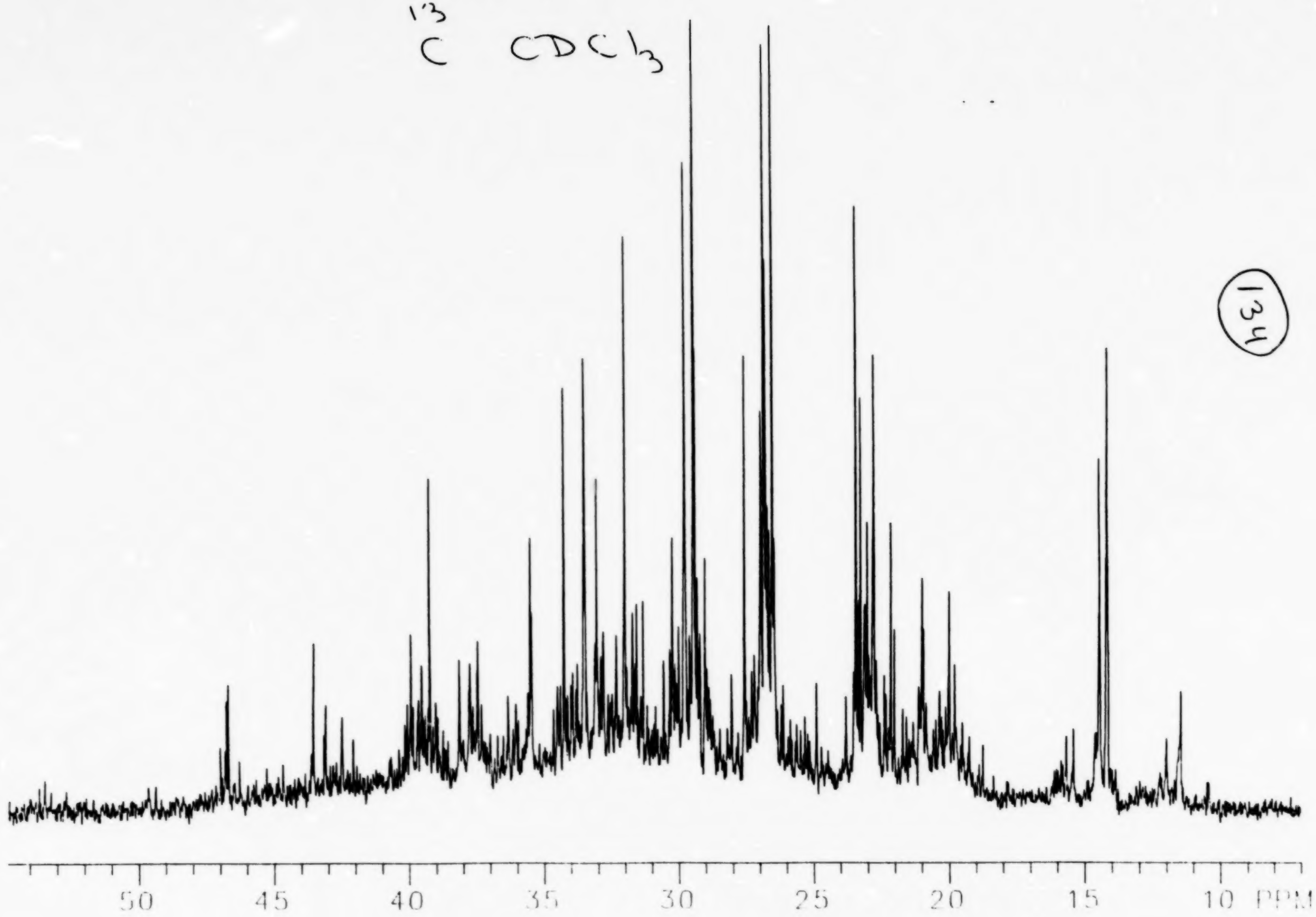


(133)



(134)

^{13}C APY CDCl$_3$



135

APS

COMMERCIAL DIESEL

$CDCl_3$

```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=     7.17
 RFL=  7898.8  RFP=  7743.0

INDEX  FREQ      PPM    INTENSITY
 01   3974.8   39.527     8.733
 02   3968.6   39.465    19.646
 03   3937.7   39.158     9.383
 04   3774.2   37.533     7.591
 05   3769.7   37.487     9.943
 06   3764.7   37.437     7.990
 07   3762.8   37.419     8.207
 08   3741.4   37.206     9.996
 09   3695.4   36.748     9.435
 10   3469.8   34.505     8.739
 11   3374.0   33.552     8.790
 12   3304.5   32.862    10.840
 13   3300.7   32.824     7.681
 14   3254.5   32.364    12.140
 15   3224.6   32.066    18.110
 16   3221.6   32.037   113.611
 17   3032.4   30.155    12.307
 18   3028.0   30.111     8.518
 19   3022.7   30.059     9.697
 20   2999.8   29.821   174.919
 21   2993.6   29.769   127.059
 22   2988.3   29.717    12.534
 23   2974.9   29.584    11.260
 24   2970.7   29.542     9.059
 25   2967.5   29.510    21.166
 26   2964.6   29.481   131.808
 27   2959.5   29.431    12.603
 28   2821.7   28.060    15.645
 29   2769.0   27.536     9.223
 30   2700.8   26.858    16.045
 31   2669.7   26.548     8.877
 32   2504.0   24.901    13.394
 33   2326.8   23.139     7.919
 34   2290.3   22.776    98.324
 35   2286.6   22.739    24.721
 36   2281.4   22.687    25.165
 37   2277.8   22.651    19.891
 38   2033.6   20.223     9.708
 39   1988.4   19.774     9.539
 40   1984.4   19.734    14.030
 41   1979.0   19.680     8.979
 42   1934.6   19.238    11.328
 43   1932.4   19.217    10.314
 44   1451.9   14.438    13.555
 45   1427.8   14.198    17.245
 46   1422.8   14.149    94.684
 47   1149.9   11.435     8.947
```

(136)

```
   ACQUISITION                                  PROCESSING
 SFRQ   100.559       DATE  29-04-86         SE        0.318
 TN      13.750       SOLVNT  CDCL3          LB        1.000
 SW     20000.0       FILE    C              RE     NOT USED
 AT       0.750                              CD     NOT USED
 NP       30016         DECOUPLING           CCD    NOT USED
 FB       11000       DN       1.750         AF     NOT USED
 BS         100       DO        74.5         FN        65536
 SS           0       DM       YYY           MATH     F
 PW        13.5       DMM     S
 P1           0       DMF       7600           SPECIAL
 D1       1.000       DHP     Y              TEMP   NOT USED
 D2           0       DLP         20         VTC        25.0
 TO           0                              PAD       0.500
 NT        1000           FLAGS              PW90       25.0
 CT        1000       IL      N
                      IN      Y
                      DP      Y
                      HS      NN
```

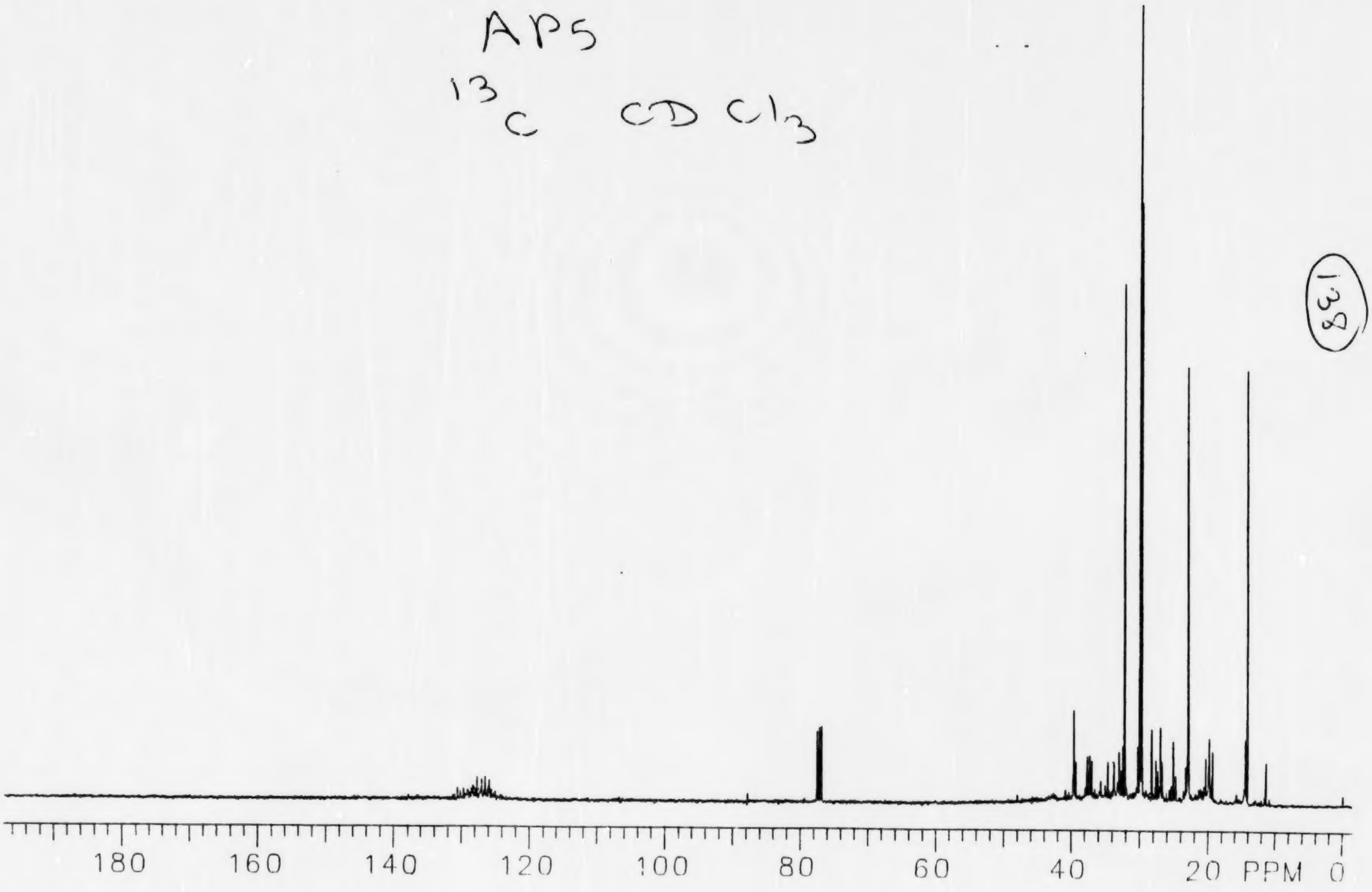
```
   ACQUISITION                                  PROCESSING
 SFRQ   100.559       DATE  29-04-86         SE        0.318
 TN      13.750       SOLVNT  CDCL3          LB        1.000
 SW     20000.0       FILE    APT            RE     NOT USED
 AT       0.750                              CD     NOT USED
 NP       30016         DECOUPLING           CCD    NOT USED
 FB       11000       DN       1.750         AF     NOT USED
 BS         100       DO        74.5         FN        65536
 SS           0       DM       YNY           MATH     F
 PW        13.5       DMM     S
 P1        27.0       DMF       7600           SPECIAL
 D1       1.000       DHP     Y              TEMP   NOT USED
 D2     7.00E-3       DLP         20         VTC        25.0
 TO           0                              PAD       0.500
 NT        1000           FLAGS              PW90       25.0
 CT        1000       IL      N
 D3     1.01E-3       IN      Y
                      DP      Y
                      HS      NN
```

```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   18.75
 RFL=  7898.8  RFP=  7743.0

INDEX  FREQ      PPM   INTENSITY
 01  13118.5  130.455   20.285
 02  13024.7  129.523   20.098
 03  12909.0  128.372   20.304
 04  12895.1  128.234   24.448
 05  12893.1  128.214   22.174
 06  12883.1  128.115   21.337
 07  12881.0  128.094   23.818
 08  12878.5  128.069   20.896
 09  12859.5  127.881   21.376
 10  12831.0  127.597   40.111
 11  12794.2  127.231   20.647
 12  12777.2  127.062   19.532
 13  12767.4  126.964   28.436
 14  12764.4  126.934   35.993
 15  12756.7  126.858   19.000
 16  12710.7  126.400   41.272
 17  12706.7  126.361   21.554
 18  12676.1  126.056   18.987
 19  12654.2  125.838   23.186
 20  12652.5  125.822   21.519
 21  12649.2  125.788   30.902
 22  12643.7  125.735   34.547
```

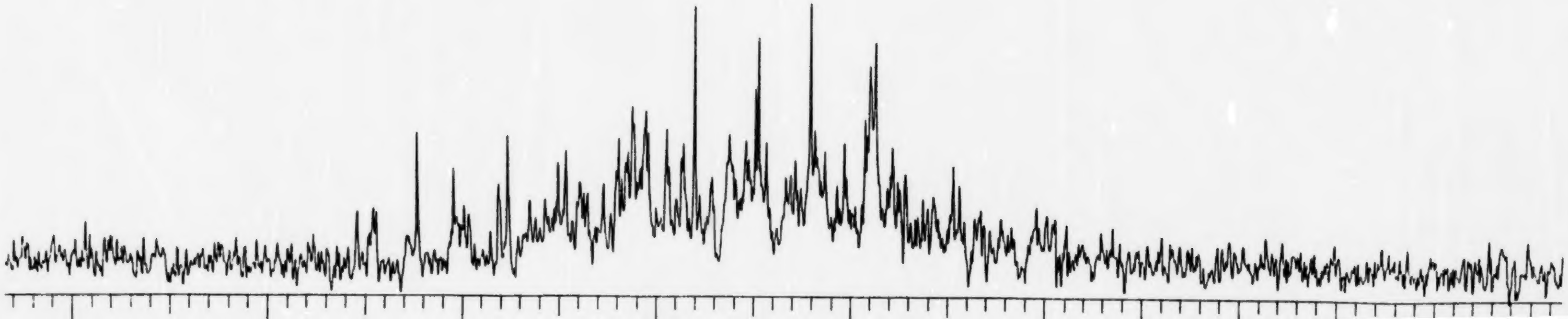
APS

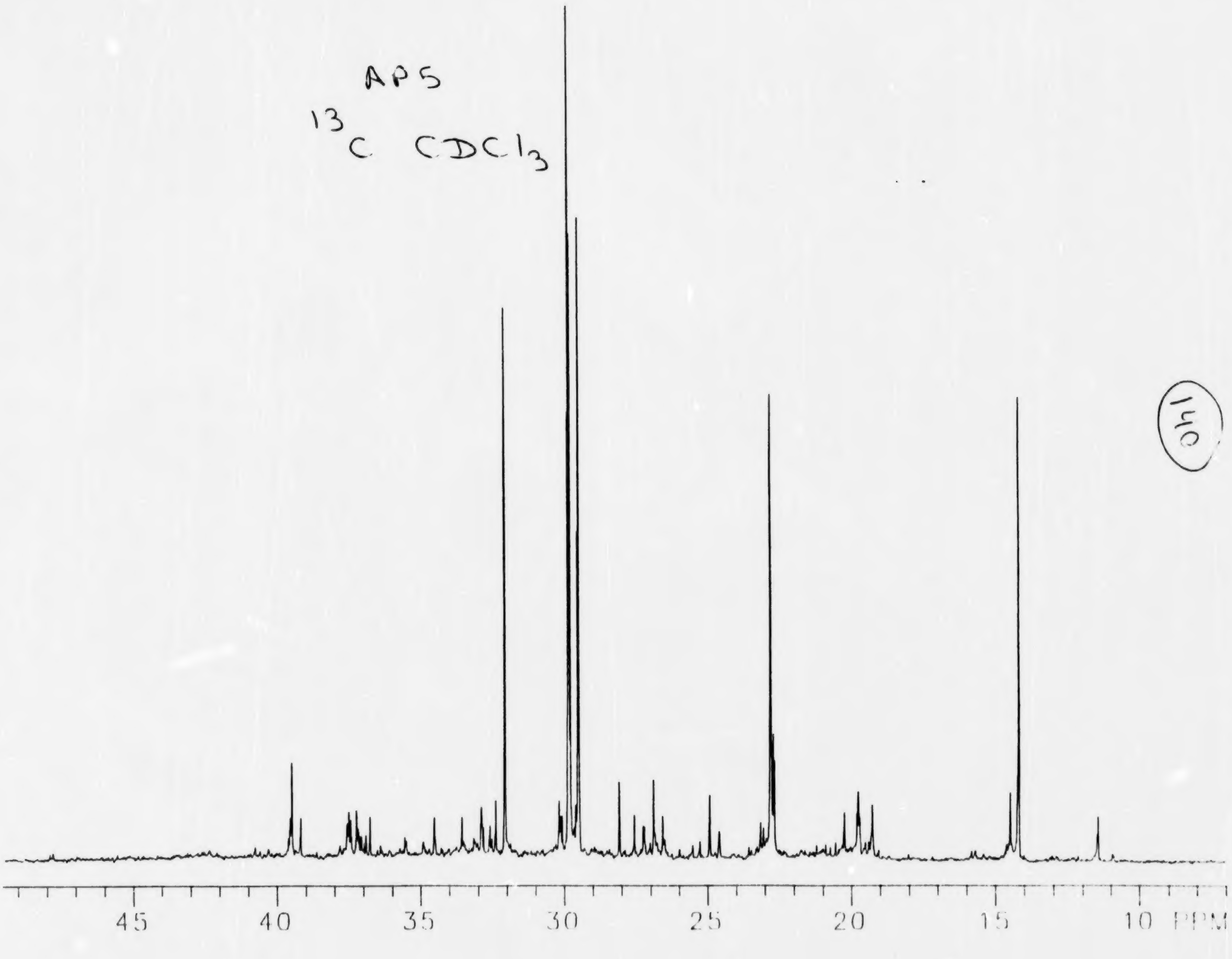
^{13}C $CDCl_3$



AP5

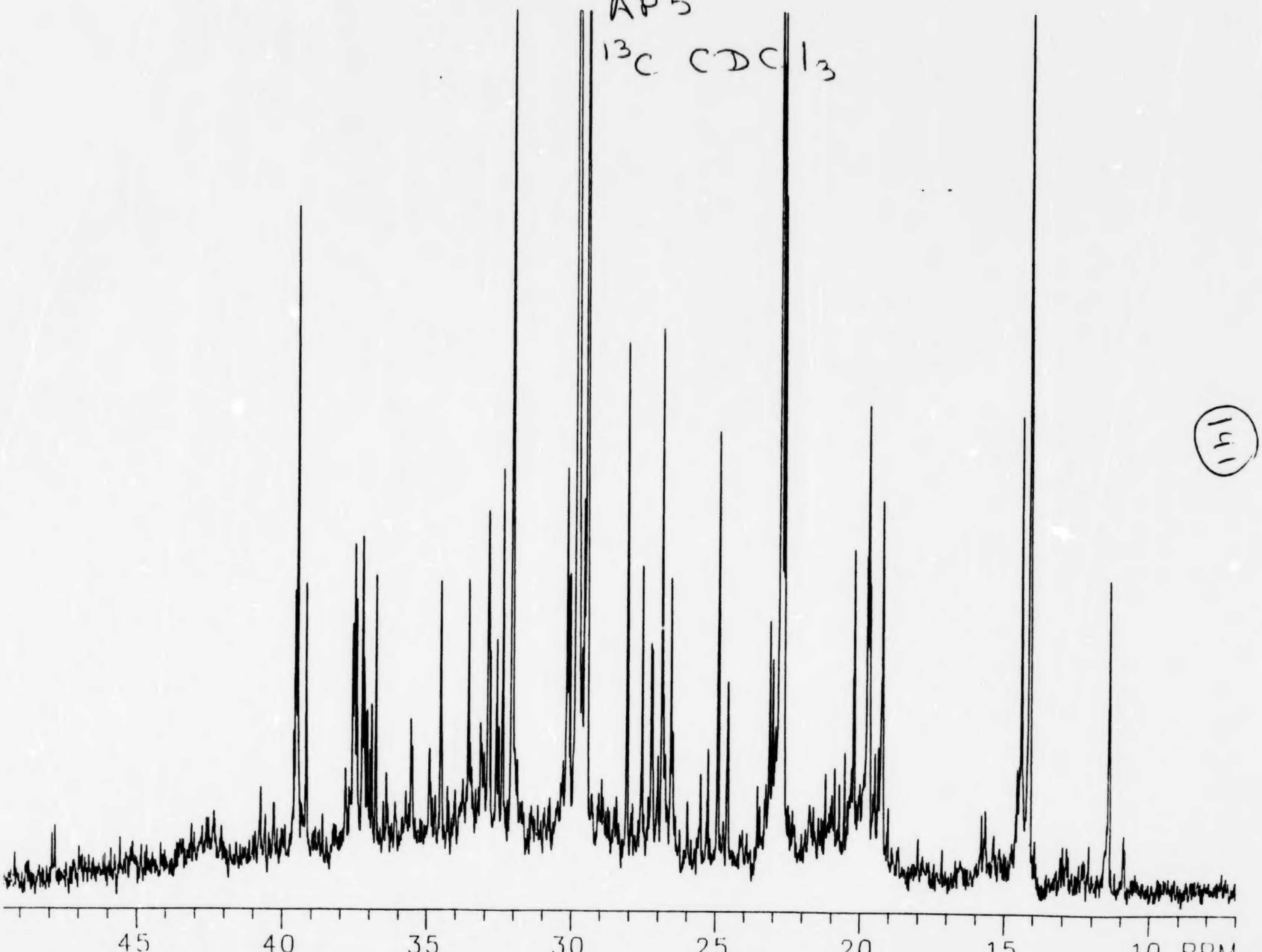
^{13}C $CDCl_3$

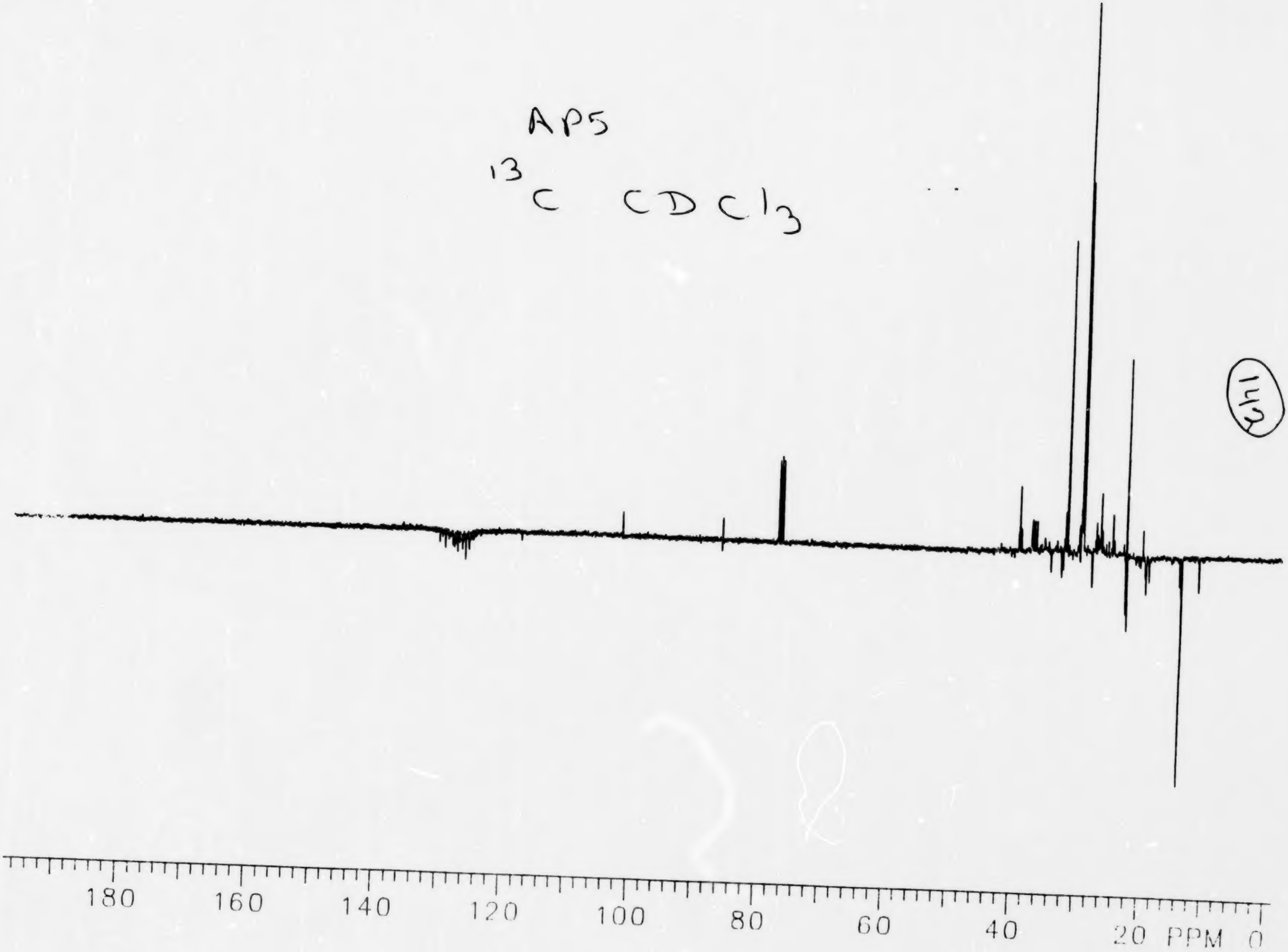




APS

^{13}C $CDCl_3$


AP5
^{13}C CDCl$_3$
45
40
35
30
25
20
15
10 PPM


AP5
^{13}C $CDCl_3$

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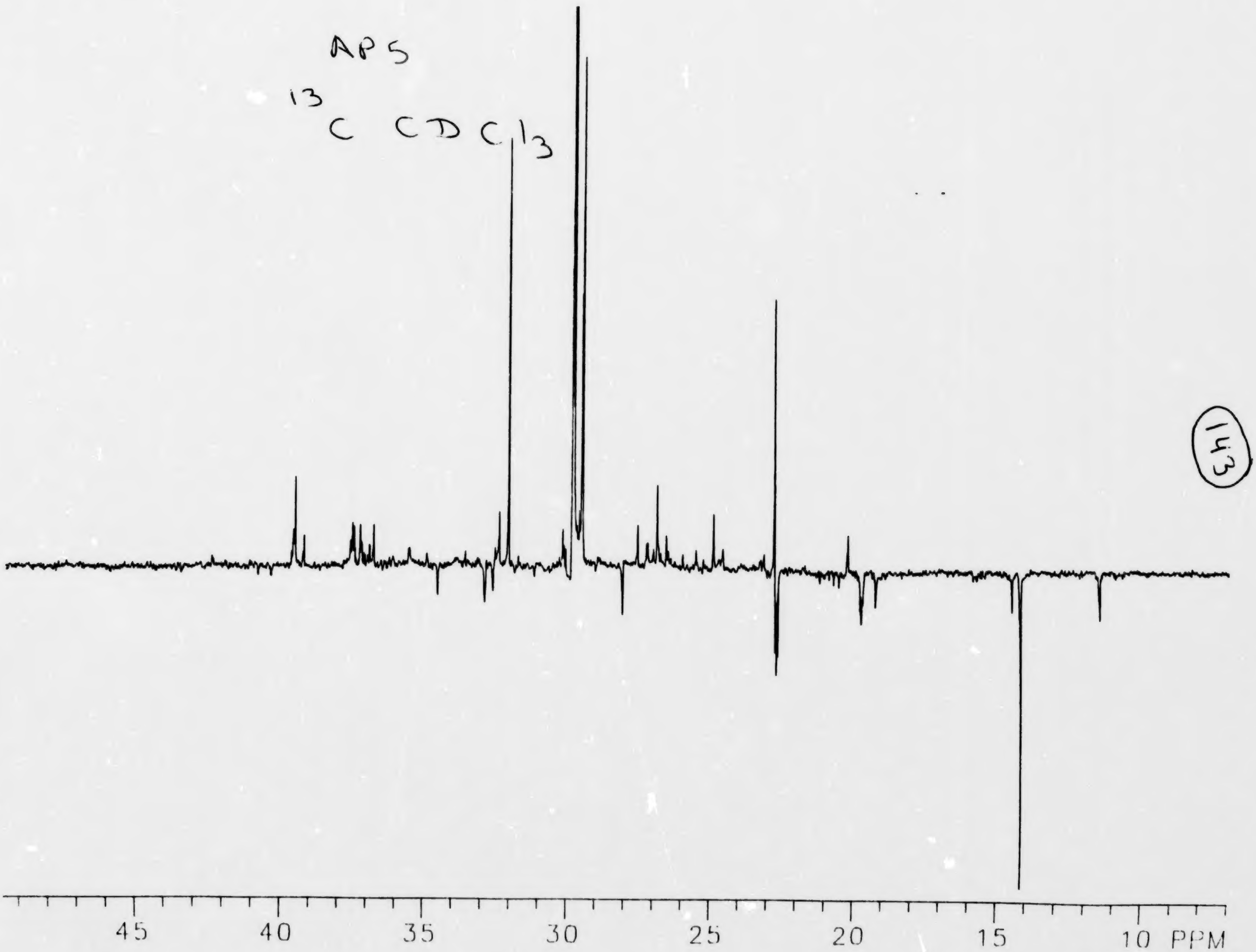

APS
^{13}C $CDCl_3$

FP5 DEPT CH only (144)

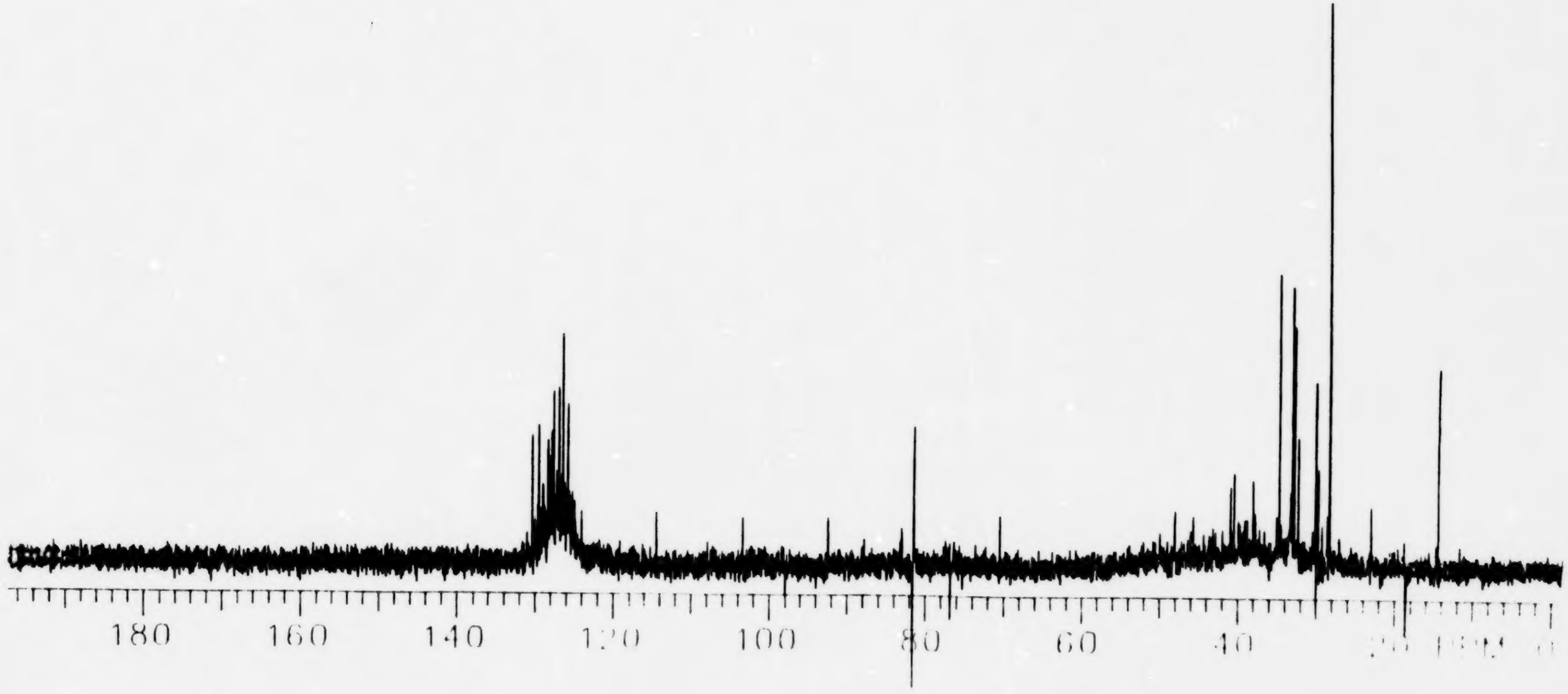
```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   14.11
 RFL=  7898.8  RFP=  7743.0

INDEX  FREQ     PPM   INTENSITY
 01   4109.7   40.868   20.417
 02   4062.3   40.397   23.564
 03   3813.0   37.918   21.808
 04   3809.7   37.885   15.608
 05   3482.0   34.626   71.428
 06   3331.6   33.131   15.387
 07   3317.8   32.994   68.242
 08   3314.5   32.961   48.608
 09   3289.8   32.715   58.736
 10   3235.4   32.174   31.717
 11   3013.4   29.966   45.948
 12   3008.2   29.914   20.602
 13   2979.2   29.626   24.203
 14   2835.8   28.200  138.248
 15   2305.8   22.930   14.738
 16   2296.8   22.840   15.282
*17   1858.8   18.484  -18.678
 18   1438.8   14.308   61.869
```

```
  ACQUISITION
SFRQ    100.559
TN       13.750
SW      20000.0
AT        0.750
NP        30016
FB        11000
BS          100
SS            0
PW         13.5
P1            0
D1        1.000
D2            0
TO            0
NT         1000
CT         1000
```

```
DATE  29-04-86
SOLVNT  CDCL3
FILE    DEPT

   DECOUPLING
DN         1.750
DO          74.5
DM        NNY
DMM       CCS
DMF         7600
DHP        Y
DLP           20
PP          35.0

      FLAGS
IL         Y
IN         Y
DP         Y
HS        NN
```

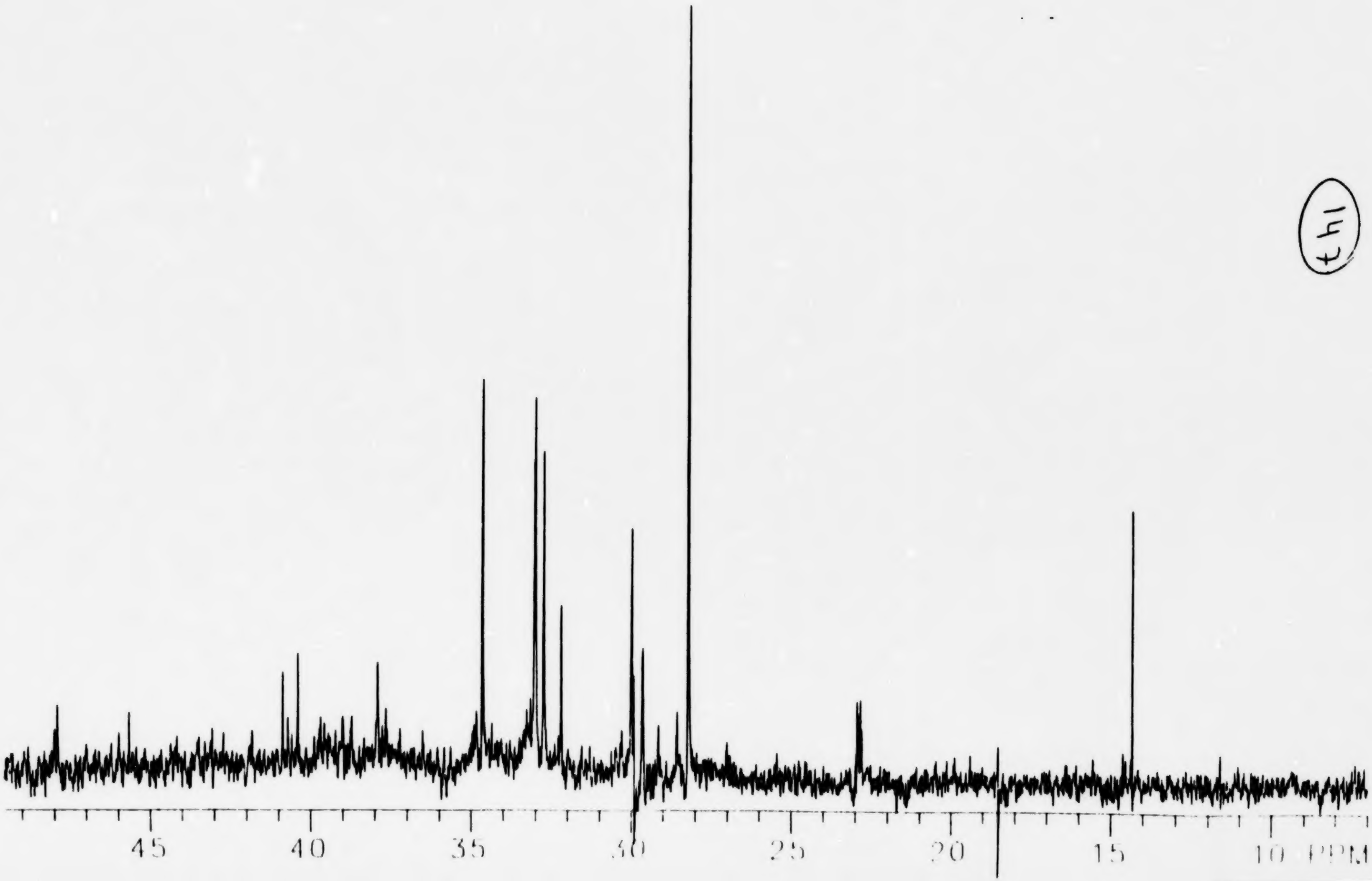
```
     PROCESSING
SE         0.318
LB         1.000
RE      NOT USED
CD      NOT USED
CCD     NOT USED
AF      NOT USED
FN         65536
MATH      F

      SPECIAL
TEMP  NOT USED
VTC         25.0
PAD        0.500
PW90        25.0
MULT       1.000
J          135.0
D3             0
```

ANS DEPT
CH ONLY



ABS DEPT
CH only

147



(148)

AP6-SC ^{13}C 25-4-86

$CDCl_3$

```
ANDARD C-13 OBSERVE
ECTRAL LINES FOR TH=   11.40
RFL=  7892.7  RFP=  7743.0

DEX  FREQ      PPM   INTENSITY
 1  13857.6  137.805   12.993
 2  12977.1  129.049  107.810
 3  12895.1  128.235   79.996
 4  12602.6  125.326   43.710
```

```
TANDARD C-13 OBSERVE
PECTRAL LINES FOR TH=   28.49
 RFL=  7892.7  RFP=  7743.0

NDEX  FREQ     PPM   INTENSITY
01    3953.3  39.314   61.227
02    3575.6  35.557   43.365
03    3570.7  35.509   31.167
04    3450.5  34.313   66.343
05    3376.4  33.576   79.520
06    3371.9  33.531   69.502
07    3328.7  33.102   46.413
08    3223.7  32.058   89.973
09    3220.8  32.029   52.638
10    3155.5  31.379   29.685
11    3044.2  30.272   45.176
12    3001.8  29.852  121.349
13    2996.6  29.799   94.526
14    2969.6  29.531   30.000
15    2966.7  29.502   88.196
16    2961.3  29.448   76.541
17    2775.5  27.601   94.665
18    2714.2  26.991   67.060
19    2703.4  26.884  125.128
20    2699.8  26.848   64.781
21    2695.3  26.833  102.809
22    2694.2  26.792   41.612
23    2691.2  26.763   41.344
24    2689.3  26.743   40.665
25    2684.6  26.697   49.477
26    2676.9  26.620   34.134
```

```
 30   2359.3   23.461   82.933
 31   2326.4   23.135   32.298
 32   2317.0   23.041   44.129
 33   2295.3   22.825   52.925
 34   2293.8   22.811   88.653
 35   2229.4   22.170   44.197
 36   2156.9   21.449   30.208
 37   2013.7   20.025   30.209
 38   1452.8   14.447   57.592
 39   1427.2   14.192   41.320
 40   1422.6   14.147   83.632
```

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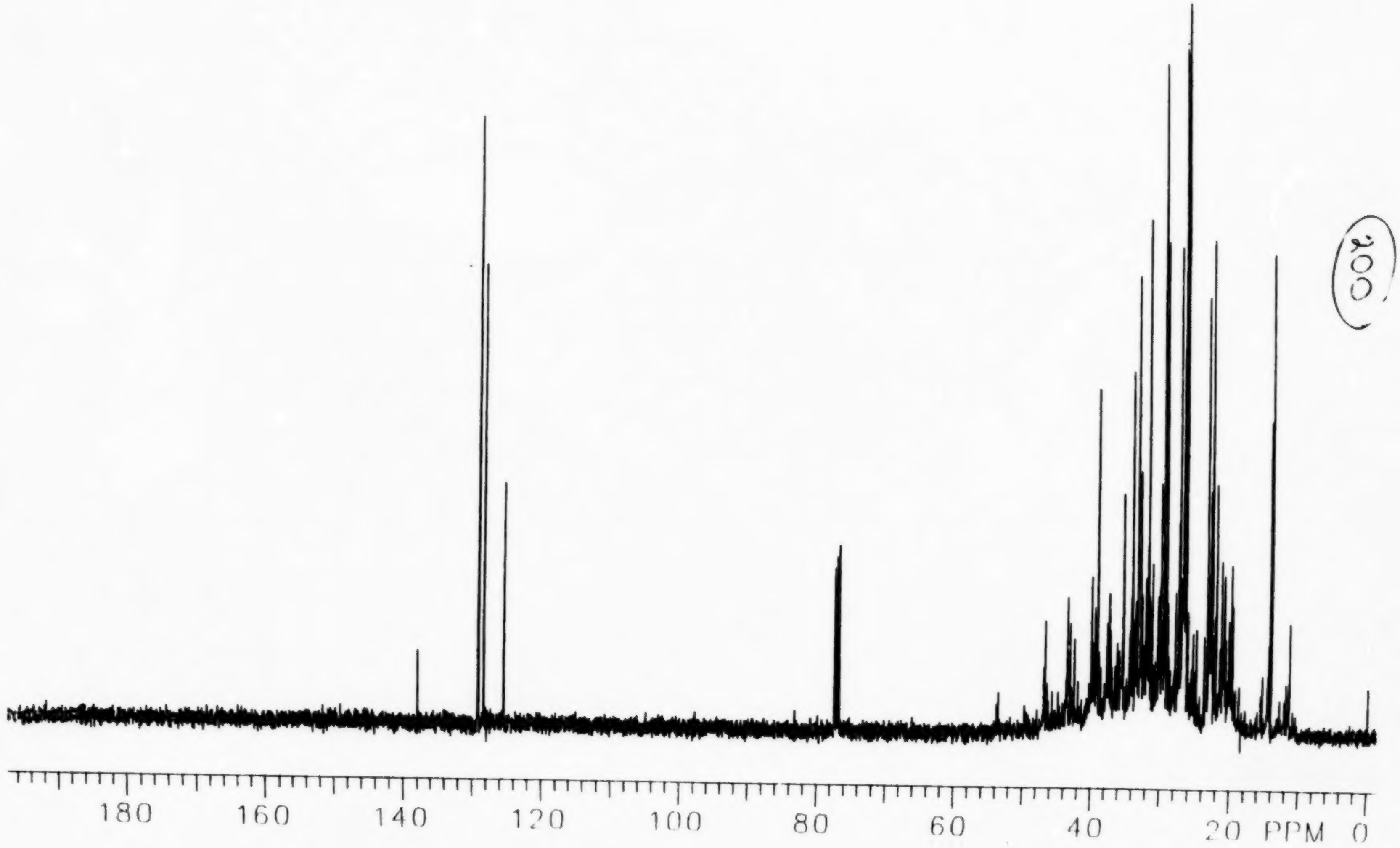
```
  ACQUISITION                                          PROCESSING
SFRQ   100.559          DATE  28-04-86              SE          0.318
TN      13.750          SOLVNT  CDCL3               LB          1.000
SW     20000.0          FILE    C                   RE       NOT USED
AT       0.750                                      CD       NOT USED
NP       30016             DECOUPLING               CCD      NOT USED
FB       11000          DN          1.750           AF       NOT USED
BS         100          DO           74.5           FN          65536
SS           0          DM         YYY              MATH      F
PW        13.5          DMM        S
P1           0          DMF          7600             SPECIAL
D1       1.000          DHP        Y                TEMP     NOT USED
D2           0          DLP            20           VTC          25.0
TO           0                                      PAD         0.500
NT         400               FLAGS                  PW90         25.0
CT         400          IL          N
                        IN          Y
                        DP          Y
                        HS          NN
```

```
  ACQUISITION                                          PROCESSING
SFRQ   100.559          DATE  28-04-86              SE          0.318
TN      13.750          SOLVNT  CDCL3               LB          1.000
SW     20000.0          FILE    APT                 RE       NOT USED
AT       0.750                                      CD       NOT USED
NP       30016             DECOUPLING               CCD      NOT USED
FB       11000          DN          1.750           AF       NOT USED
BS         100          DO           74.5           FN          65536
SS           0          DM         YNY              MATH      F
PW        13.5          DMM        S
P1        27.0          DMF          7600             SPECIAL
D1       1.000          DHP        Y                TEMP     NOT USED
D2     7.00E-3          DLP            20           VTC          25.0
TO           0                                      PAD         0.500
NT        1000               FLAGS                  PW90         25.0
CT        1000          IL          N
D3     1.01E-3          IN          Y
                        DP          Y
```

APG (SC)

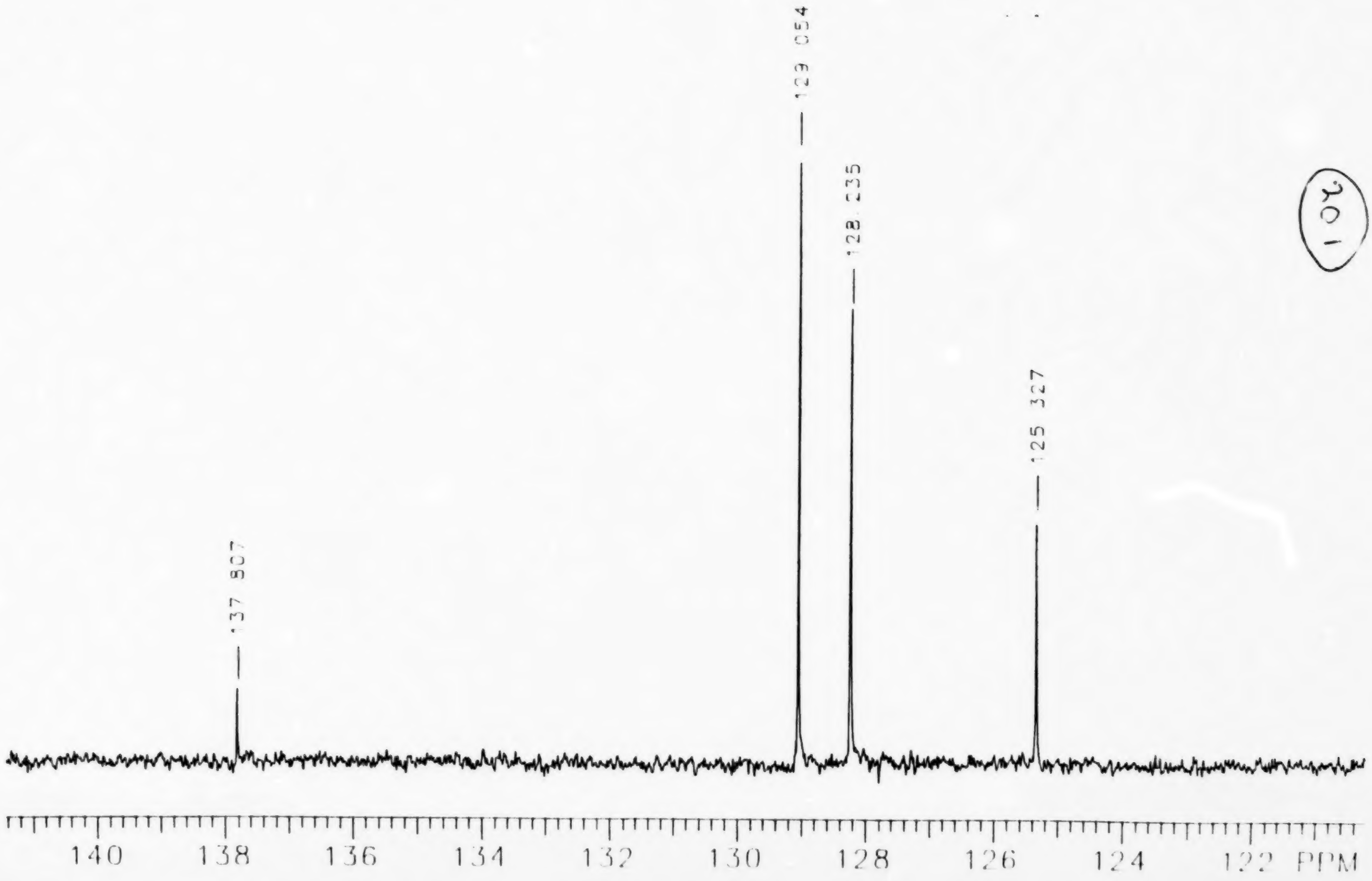
^{13}C $CDCl_3$

200

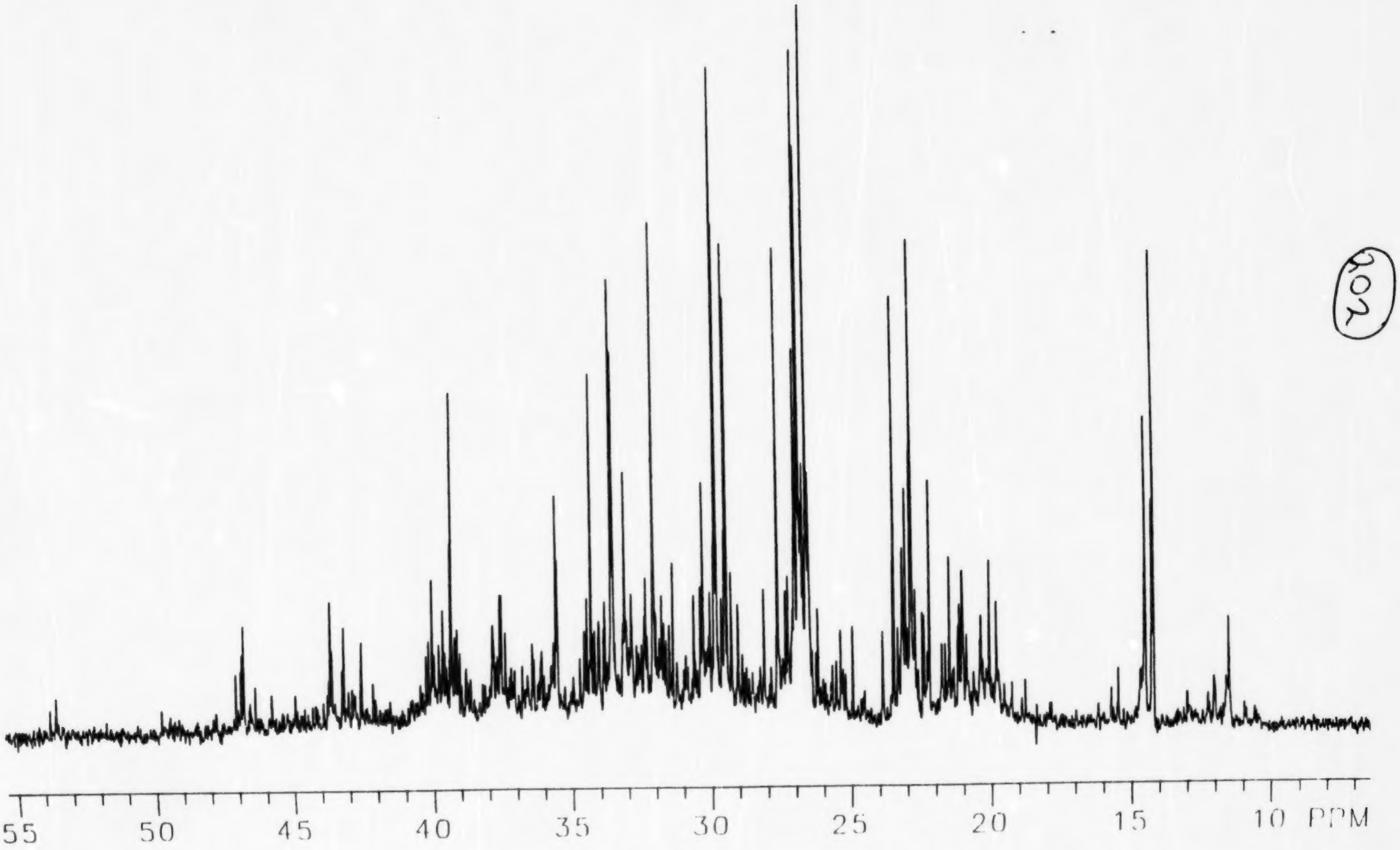


AP6-(SC)

^{13}C $CDCl_3$

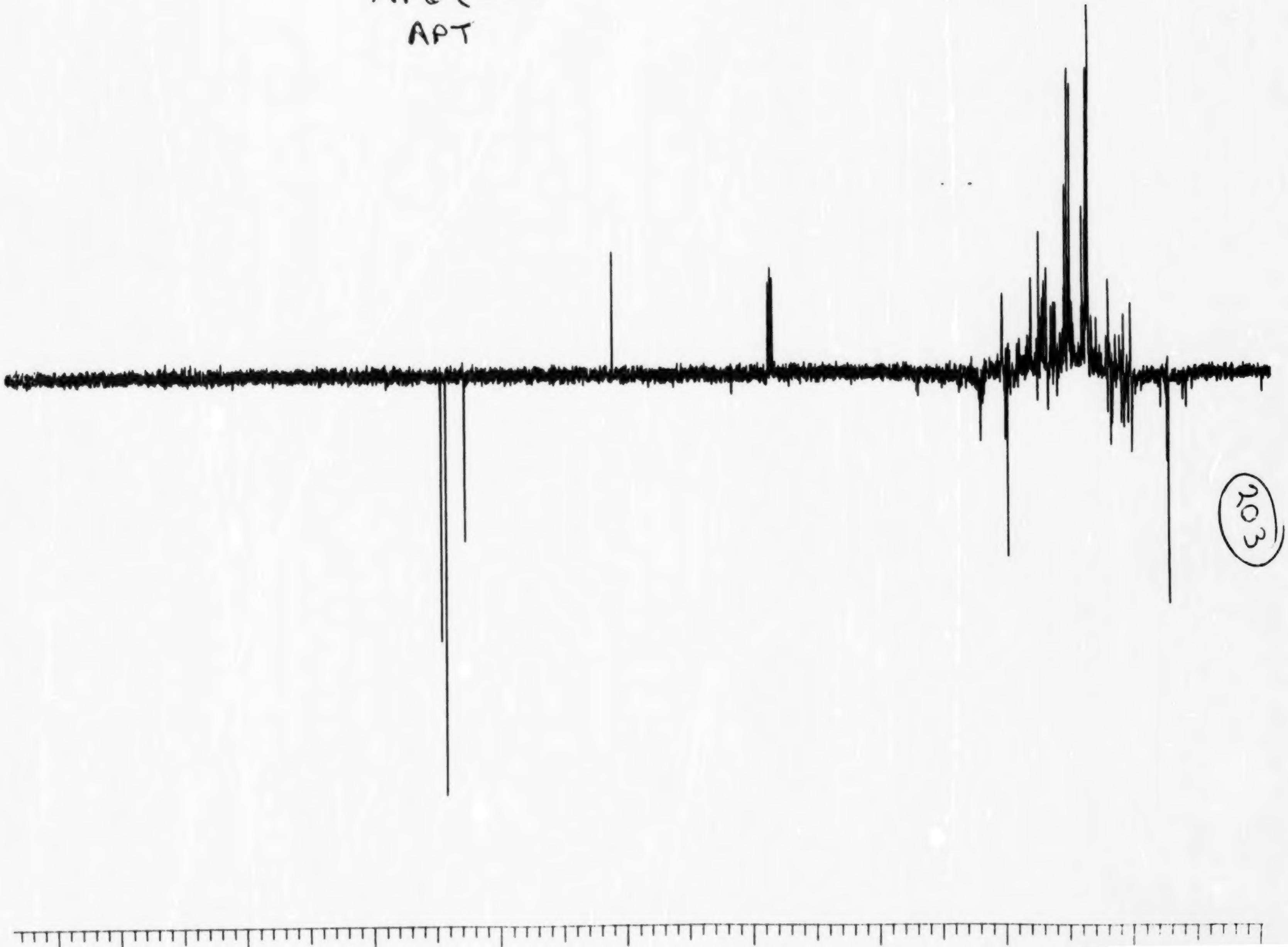


AP6-(SC)
^{13}C $CDCl_3$



(203)

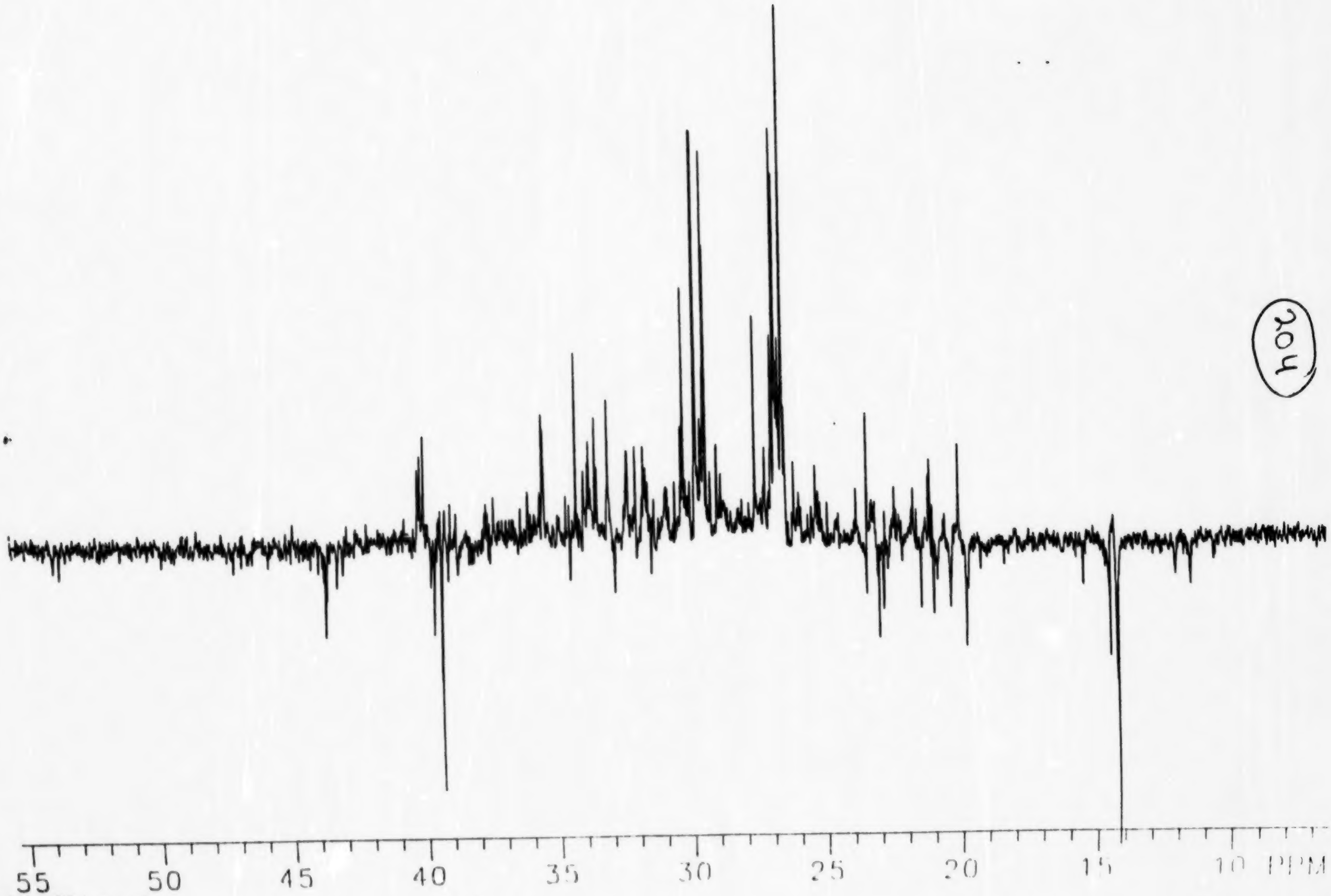
AP6 (5C)
APT



AP6(5C) APT

AP6 (5C)

^{13}C $CDCl_3$



HBHB CDCl$_3$ ^{13}C 205

```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   16.66
 RFL=  7903.7  RFP=  7743.0

INDEX  FREQ      PPM   INTENSITY
 01  13778.3  137.018   17.437
 02  13038.6  129.661  113.821
 03  12989.6  129.174   18.275
 04  12980.5  129.084   68.379
 05  12971.1  128.990   45.301
 06  12953.7  128.817   22.214
 07  12943.2  128.713   24.956
 08  12940.6  128.687   54.162
 09  12894.5  128.228   18.249
 10  12789.5  127.185   43.878
 11  12782.9  127.118   46.247
 12  12768.8  126.978   27.762
 13  12761.2  126.903   17.601
 14  12751.1  126.802   21.456
 15  12747.5  126.766   20.939
 16  12697.4  126.268   25.527
 17  12694.5  126.239   48.690
 18  12665.2  125.948   19.062
 19  12606.9  125.368  105.016
 20  12576.7  125.067   25.236
 21  12383.2  123.143   57.382
 22  11951.5  118.851   98.792
```

```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   71.46
 RFL=  7903.7  RFP=  7743.0

INDEX  FREQ      PPM   INTENSITY
 01   6625.4   65.886  117.702
```

```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   34.40
```

```
2  11951.5  118.851   98.792
```

206

```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   71.46
 RFL=  7903.7  RFP=  7743.0

INDEX  FREQ      PPM   INTENSITY
 01   6625.4   65.886  117.702
```

```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   34.48
 RFL=  7903.7  RFP=  7743.0

INDEX  FREQ      PPM   INTENSITY
 01    3943.9   39.220   62.274
 02    3566.8   35.470   44.989
 03    3562.0   35.422   36.303
 04    3441.7   34.226   69.530
 05    3368.7   33.500   73.599
 06    3364.2   33.455   71.661
 07    3321.0   33.025   54.074
 08    3215.1   31.973   89.997
 09    3171.6   31.540   36.225
 10    3035.6   30.187   48.565
 11    2992.3   29.756  111.759
 12    2988.1   29.715   89.032
 13    2958.2   29.417   92.640
 14    2953.9   29.375  133.251
 15    2944.9   29.285   40.656
 16    2914.9   28.987   41.060
 17    2767.6   27.522   77.284
 18    2707.1   26.921   73.141
 19    2695.3   26.803  126.921
 20    2691.7   26.767   80.143
 21    2690.1   26.752  104.142
 22    2686.2   26.713   47.963
 23    2683.6   26.687   58.965
 24    2676.9   26.620   51.548
 25    2664.3   26.495  133.381
 26    2657.3   26.425   55.853
 27    2352.1   23.391  103.210
 28    2345.5   23.325   37.730
 29    2337.2   23.242   69.507
 30    2318.5   23.056   38.116
 31    2312.1   22.992   49.096
 32    2285.6   22.729   91.754
 33    2222.0   22.096   45.187
```

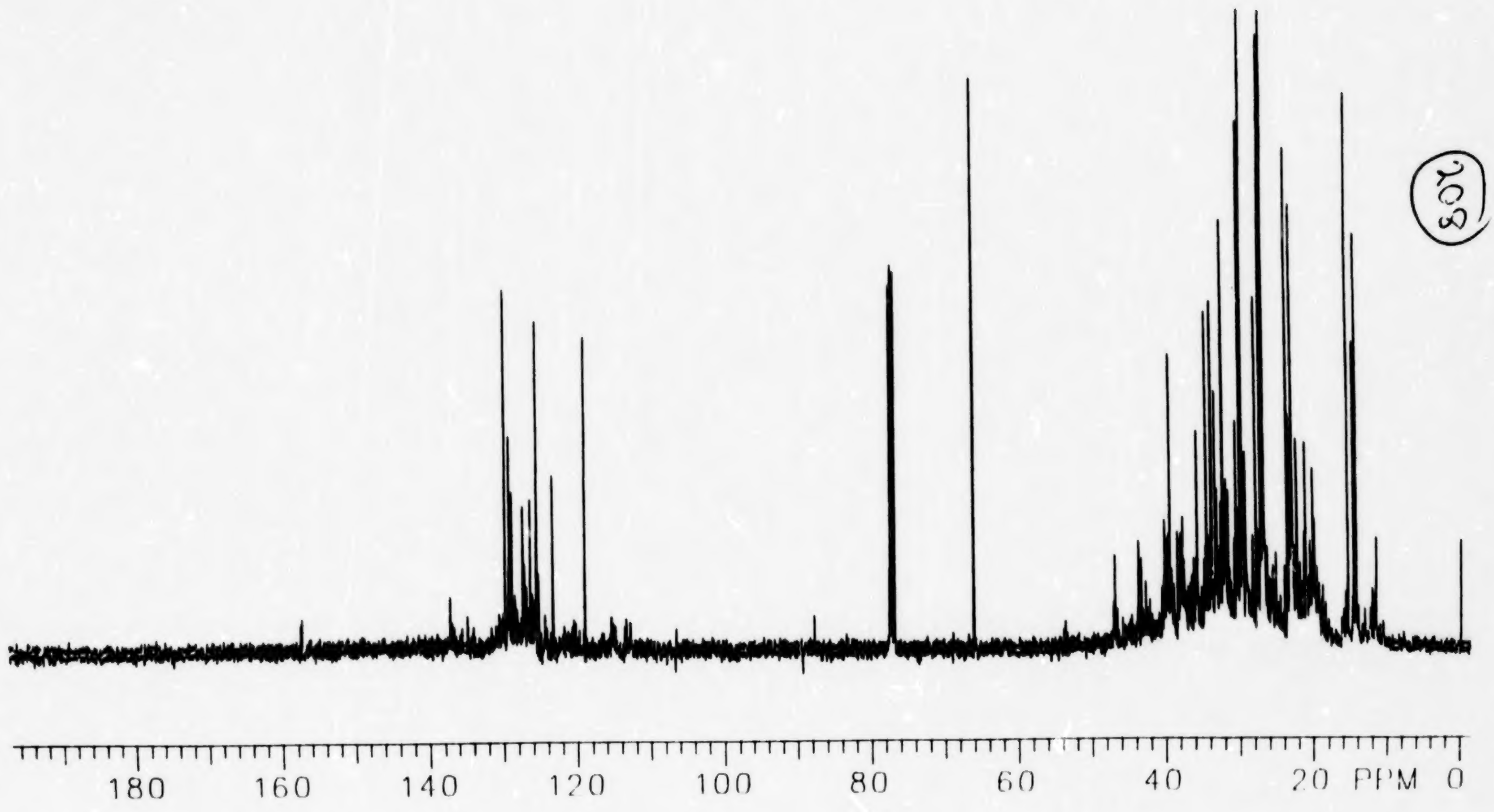
```
34  2209.5  21.970   37.589
35  2104.4  20.927   42.617
36  2005.8  19.946   38.054
37  1528.5  15.200  118.486
38  1447.8  14.397   64.133
39  1422.1  14.142   44.428
40  1417.5  14.096   80.794
```

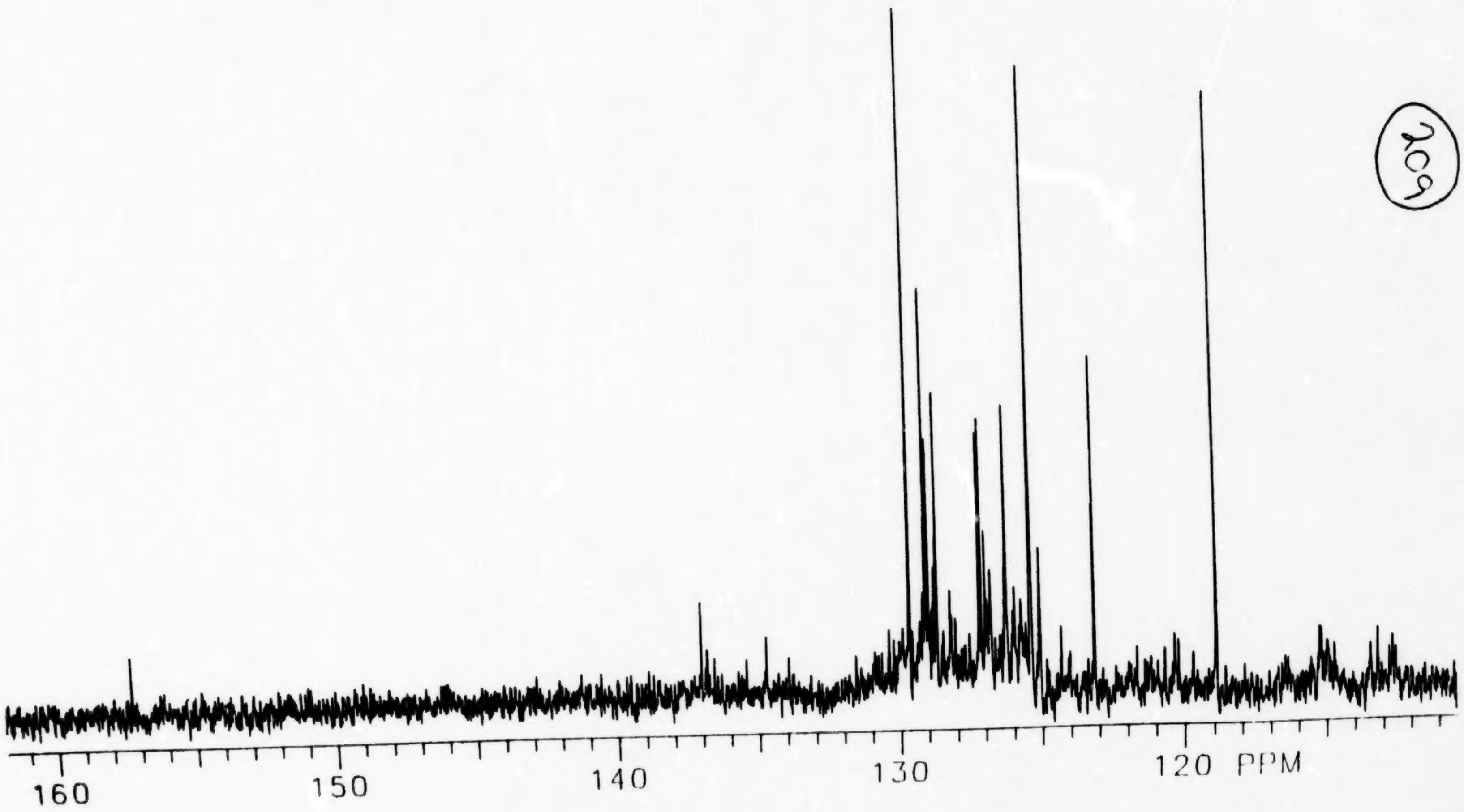
```
  ACQUISITION                                        PROCESSING
SFRQ   100.559        DATE  05-05-86            SE        0.318
TN      13.750        SOLVNT  CDCL3             LB        1.000
SW     20000.0        FILE    C                 RE     NOT USED
AT       0.750                                  CD     NOT USED
NP       30016           DECOUPLING             CCD    NOT USED
FB       11000        DN         1.750          AF     NOT USED
BS         100        DO          74.5          FN        65536
SS           0        DM         YYY            MATH    F
PW        13.5        DMM      S
P1           0        DMF         7600             SPECIAL
D1       1.000        DHP      Y                TEMP   NOT USED
D2           0        DLP           20          VTC        25.0
TO           0                                  PAD       0.500
NT        2000             FLAGS                PW90       25.0
CT        1241        IL       N
                      IN       Y
                      DP       Y
                      HS       NN
```

H·B4B

^{13}C $CDCl_3$

208



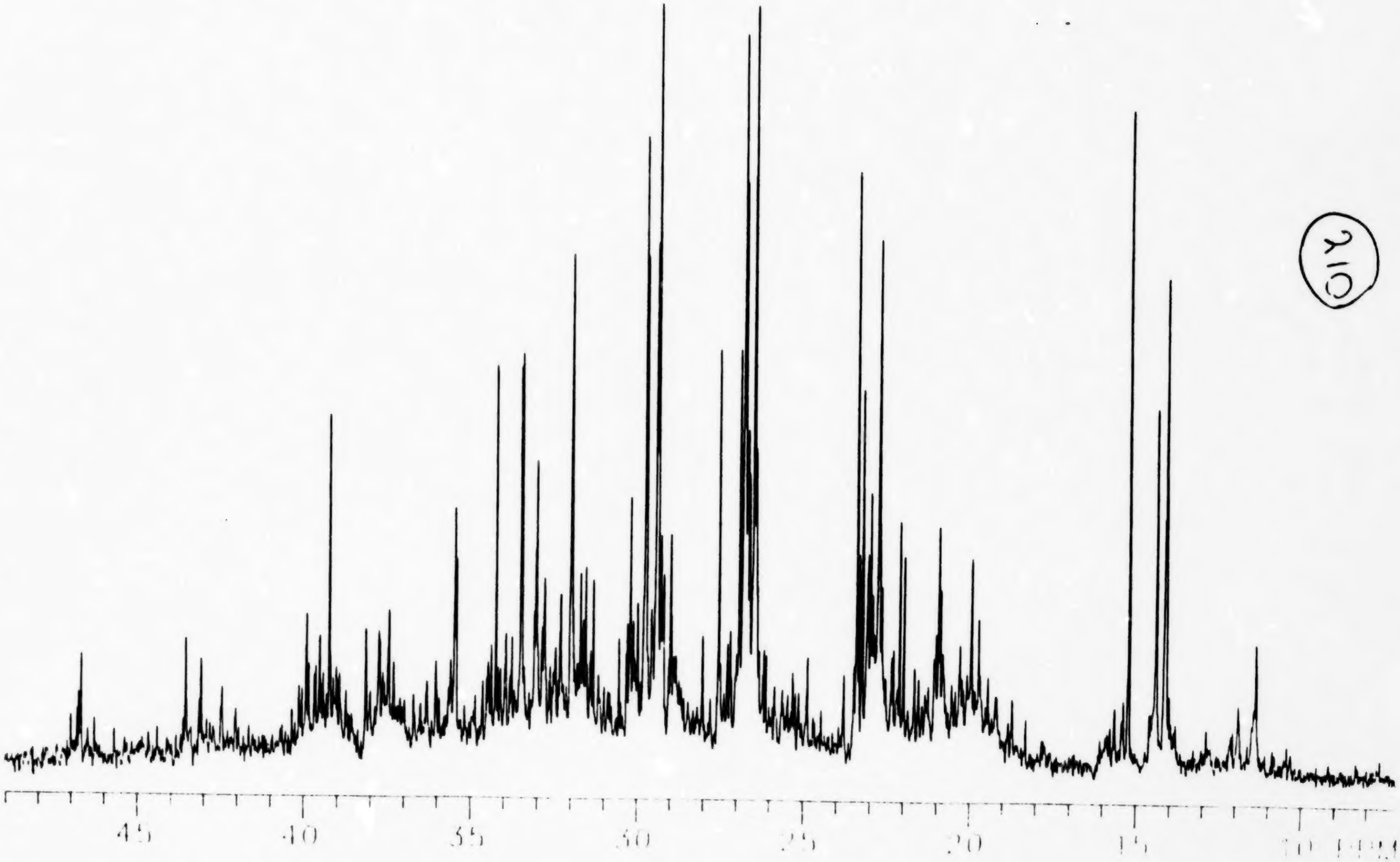


H·B4 B

^{13}C $CDCl_3$

H·B4B

^{13}C $CDCl_3$



HBHB CDCl$_3$ ^{13}C APT (211)

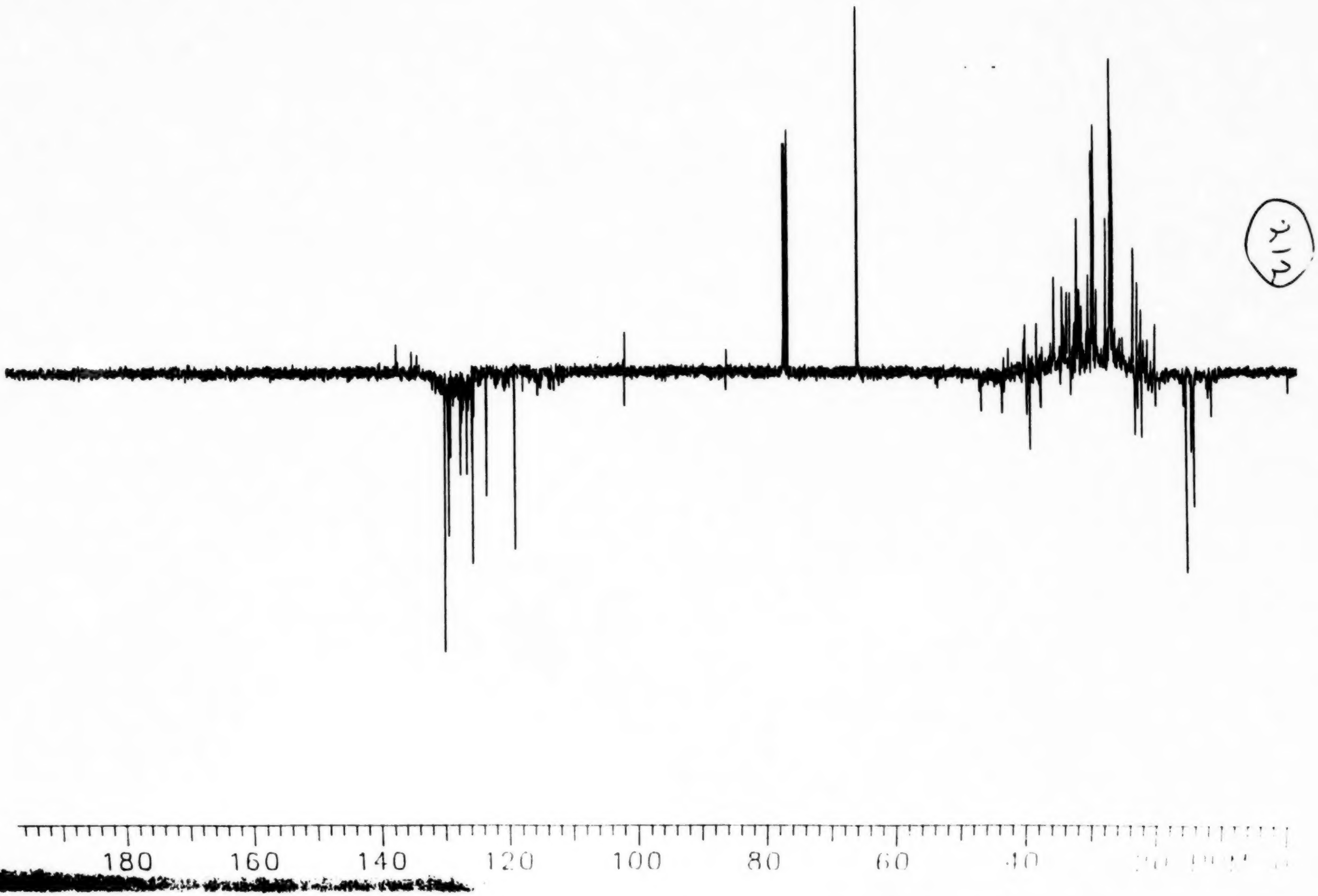
CH$_3$, CH - down

CH$_2$, C - up

```
  ACQUISITION                                   PROCESSING
SFRQ   100.559        DATE  05-05-86        SE        0.318
TN      13.750        SOLVNT  CDCL3         LB        1.000
SW     20000.0        FILE    APT           RE     NOT USED
AT       0.750                              CD     NOT USED
NP       30016           DECOUPLING         CCD    NOT USED
FB       11000        DN         1.750      AF     NOT USED
BS         100        DO          74.5      FN        65536
SS           0        DM         YNY        MATH      F
PW        13.5        DMM        S
P1        27.0        DMF         7600         SPECIAL
D1       1.000        DHP        Y          TEMP   NOT USED
D2     7.00E-3        DLP           20      VTC        25.0
TO           0                              PAD       0.500
NT        2000            FLAGS             PW90       25.0
CT        2000        IL         N
D3     1.01E-3        IN         Y
                      DP         Y
                      HS         NN
```

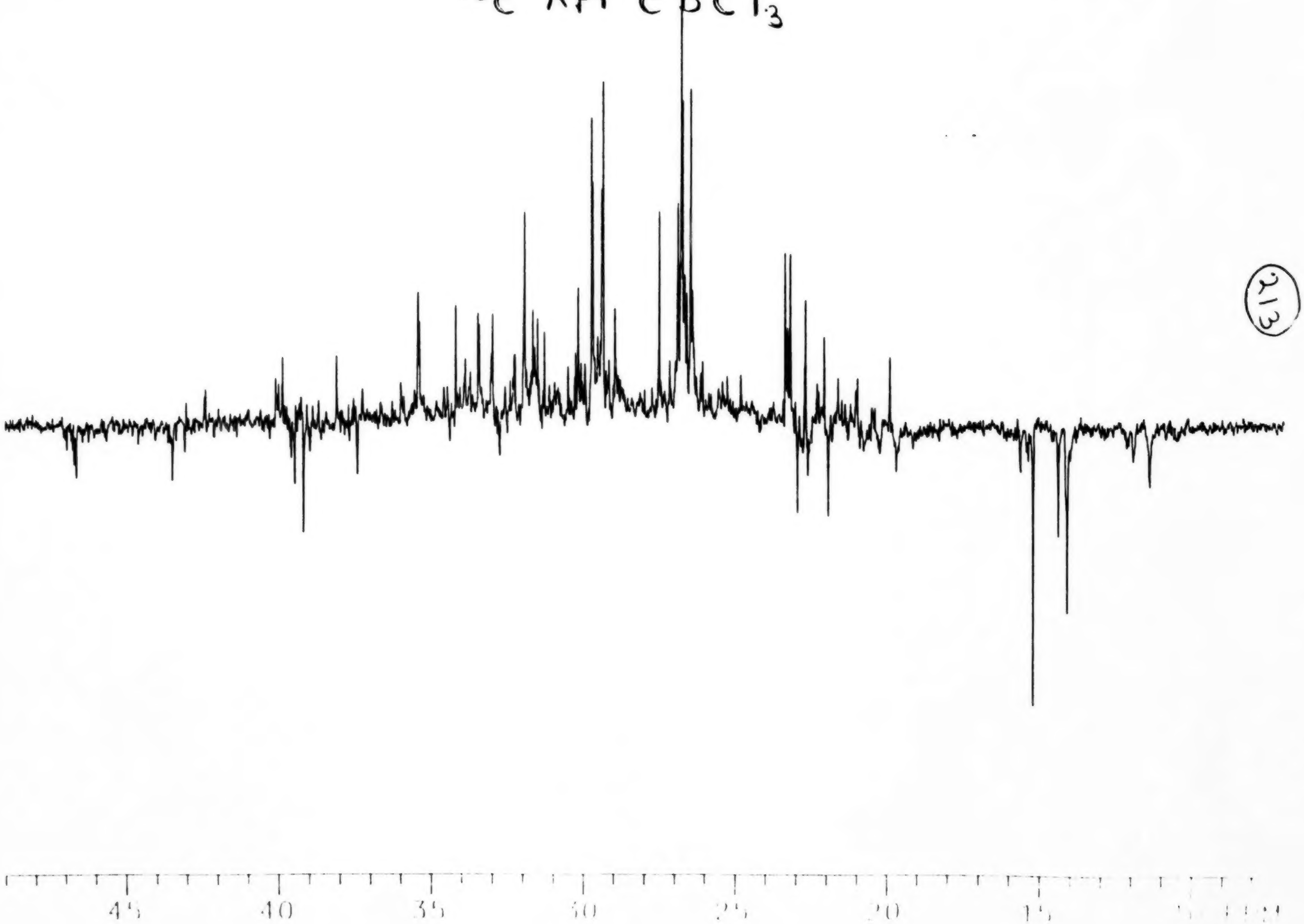
HB4B

^{13}C APT $CDCl_3$

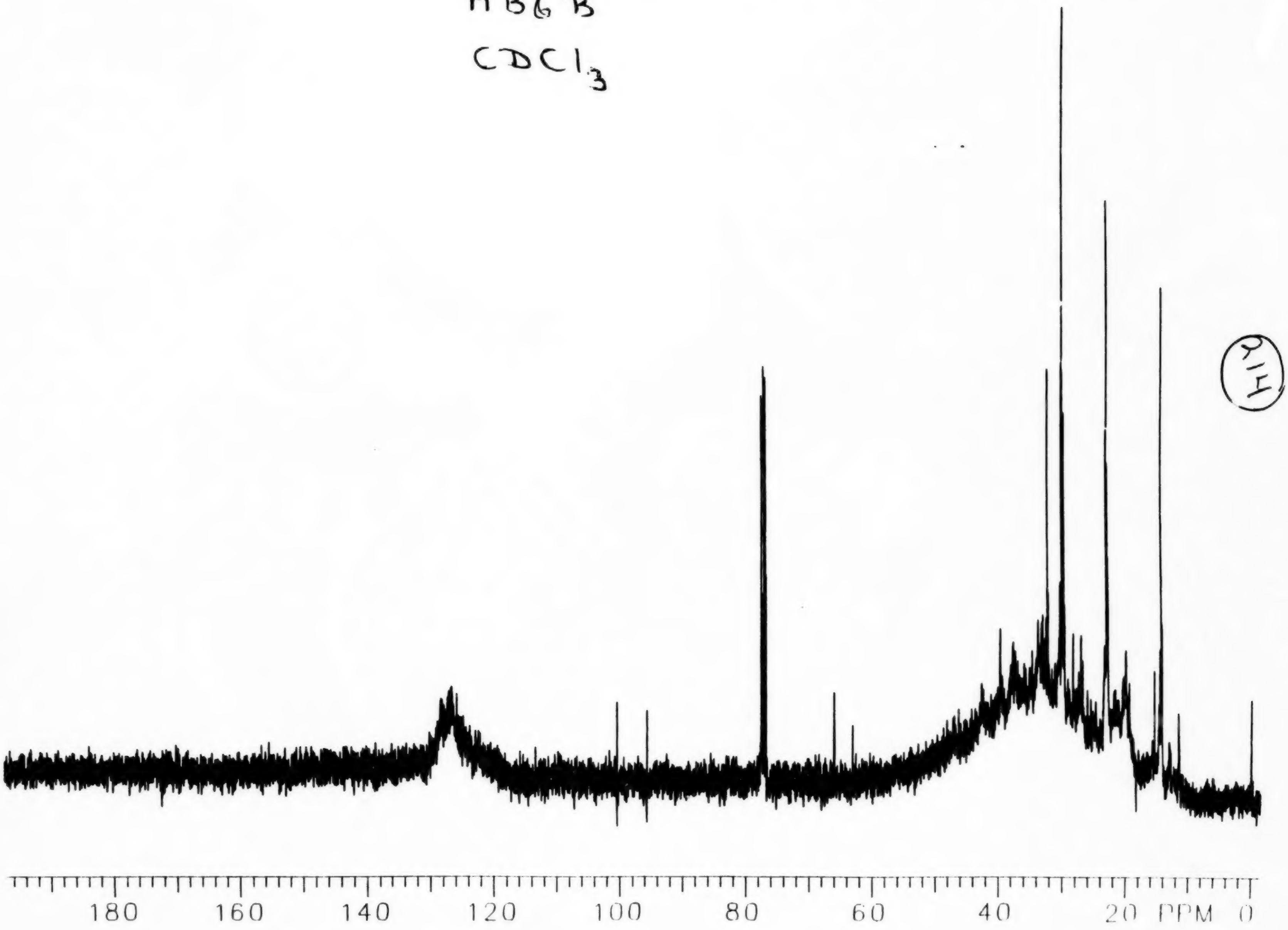


HB4B

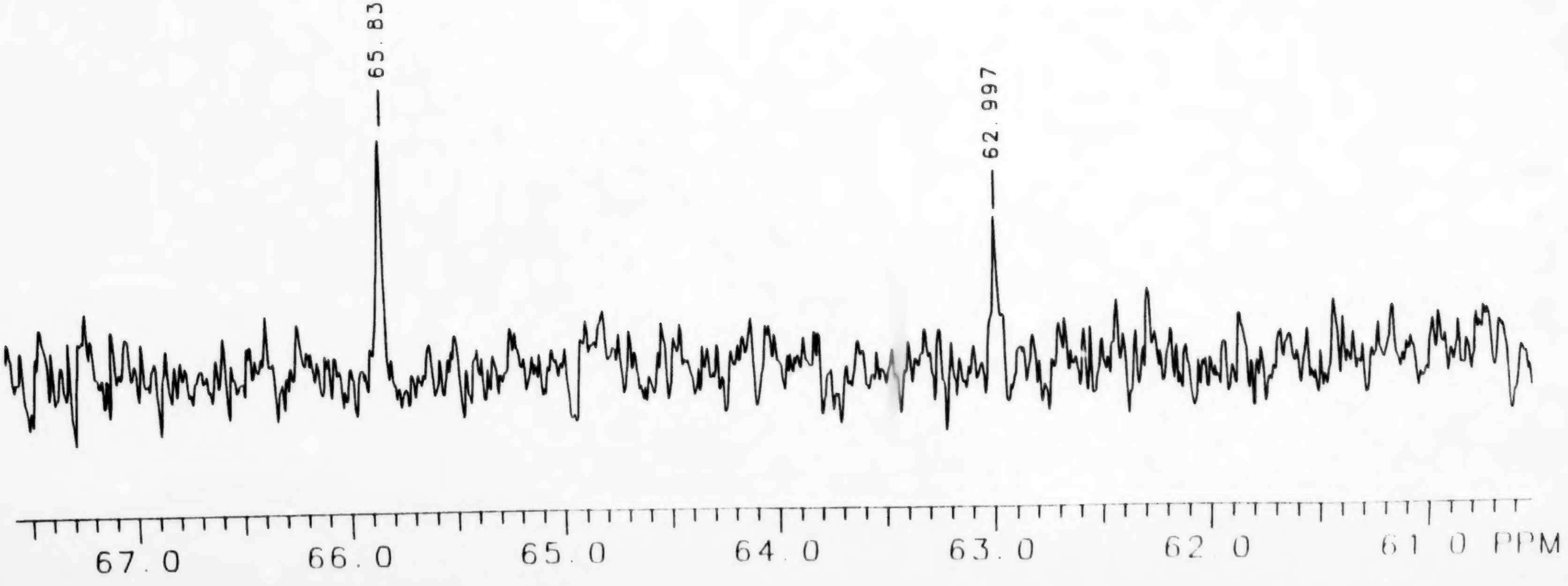
^{13}C APT $CDCl_3$

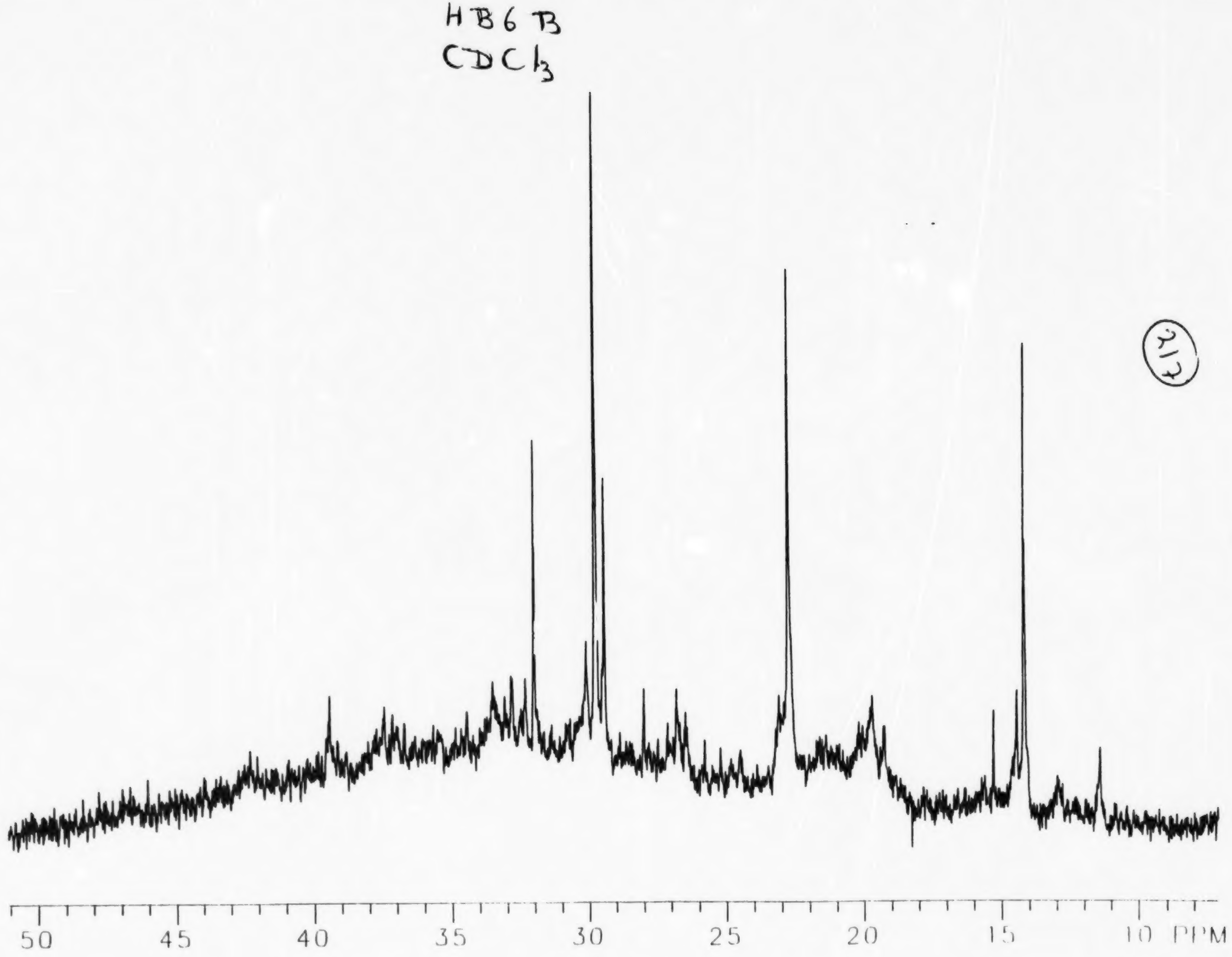


HB6B
$CDCl_3$



HB6 B
$CDCl_3$




HB6B
CDCl3
50
45
40
35
30
25
20
15
10 PPM

(218)

```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   16.50
 RFL=  7900.0  RFP=  7743.0

INDEX  FREQ      PPM   INTENSITY
 01   6619.9   65.831   90.578
 02   6333.7   62.984   20.675
```

```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   16.50
 RFL=  7900.0  RFP=  7743.0

INDEX  FREQ      PPM   INTENSITY
 01   2283.7   22.710   92.405
 02   2011.5   20.003   17.032
 03   1977.3   19.663   22.742
 04   1933.6   19.229   18.415
 05   1533.7   15.252   30.855
 06   1450.1   14.420   21.923
 07   1420.8   14.129   95.575
 08   1147.2   11.408   17.241
```

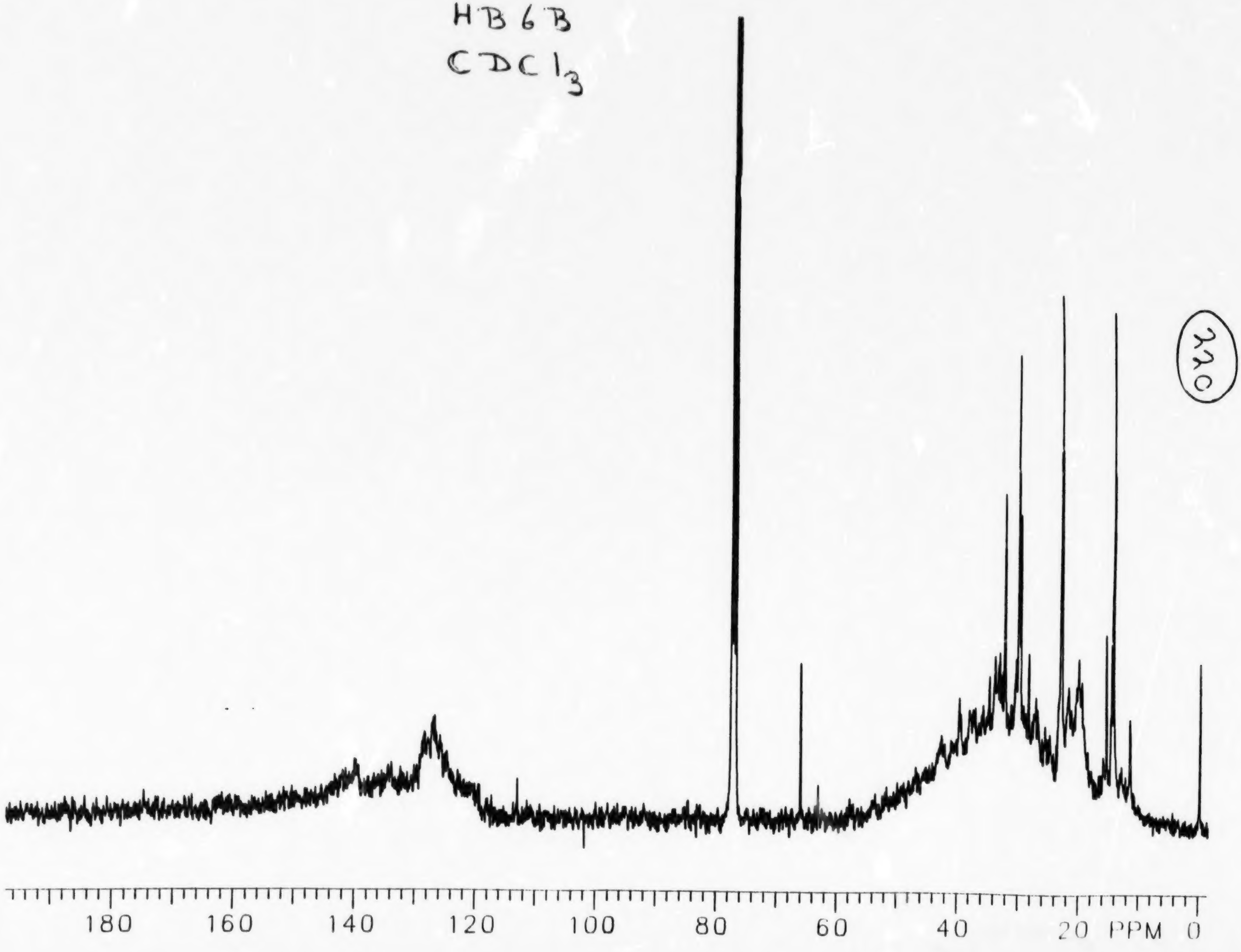
```
STANDARD C-13 OBSERVE
SPECTRAL LINES FOR TH=   16.50
 RFL=  7900.0  RFP=  7743.0

INDEX  FREQ      PPM   INTENSITY
 01   1533.7   15.252   30.582
 02   1450.1   14.420   21.576
 03   1420.8   14.129   96.219
 04   1147.2   11.408   16.989
```

```
  ACQUISITION                                     PROCESSING
SFRQ   100.559          DATE  12-05-86          SE          0.064
```

```
                                                  PROCESSING
 ACQUISITION                                    SE        0.064
SFRQ  100.559          DATE  12-05-86           LB        5.000
TN     13.750          SOLVNT  CDCL3            RE     NOT USED
SW    20000.0          FILE    C                CD     NOT USED
AT      0.819                                   CCD    NOT USED
NP      32768            DECOUPLING             AF     NOT USED
FB      11000          DN         1.750         FN        65536
BS        100          DO          74.5         MATH     F
SS          0          DM        NNY
PW       13.5          DMM       S                 SPECIAL
P1          0          DMF         7600          TEMP  NOT USED
D1     10.000          DHP       Y               VTC       25.0
D2          0          DLP           20          PAD      0.500
TO          0                                    PW90      25.0
NT       1000               FLAGS
CT        662          IL        N
                       IN        Y
                       DP        N
                       HS        NN
```

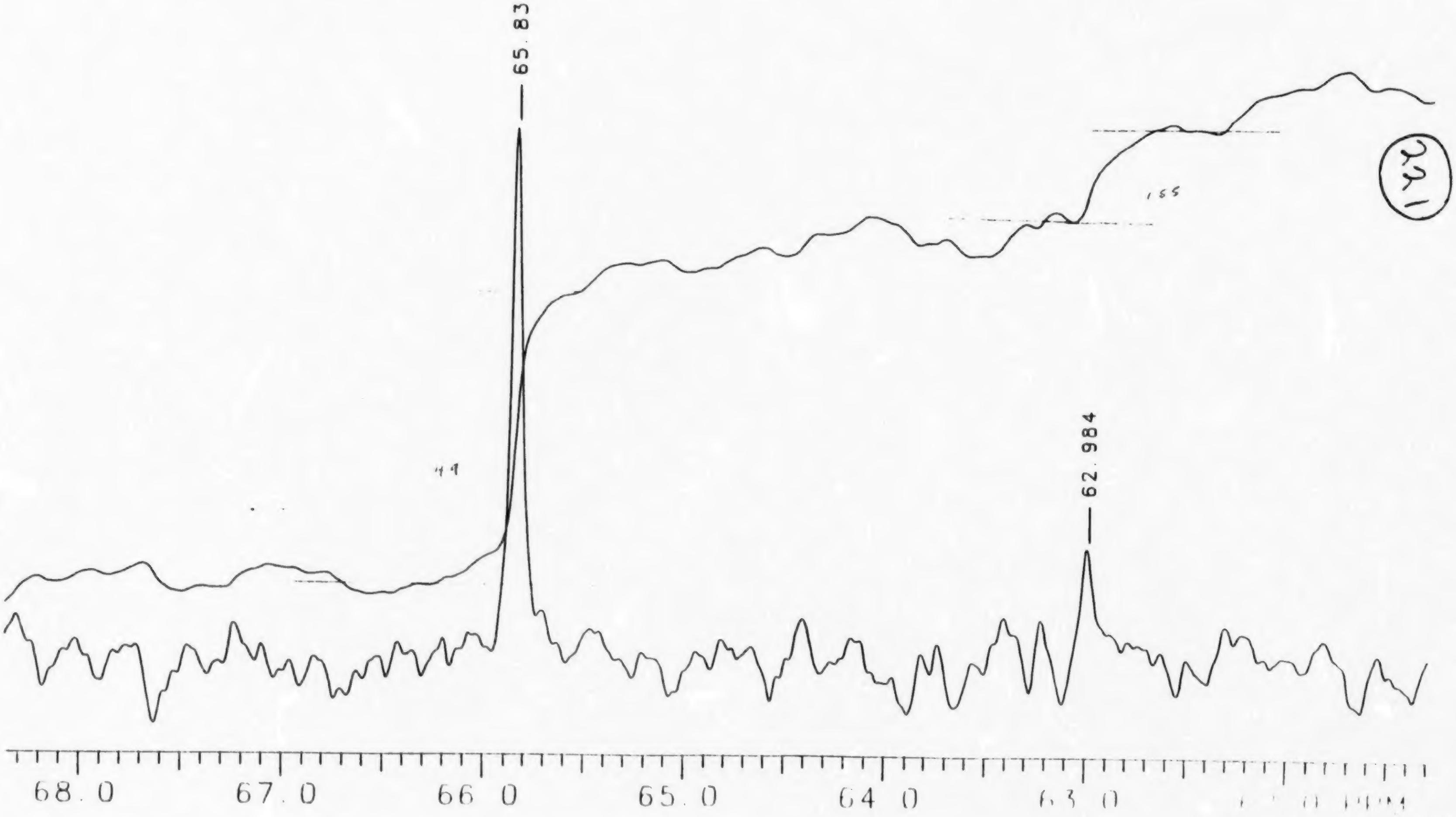
HB 6B
$CDCl_3$

(220)



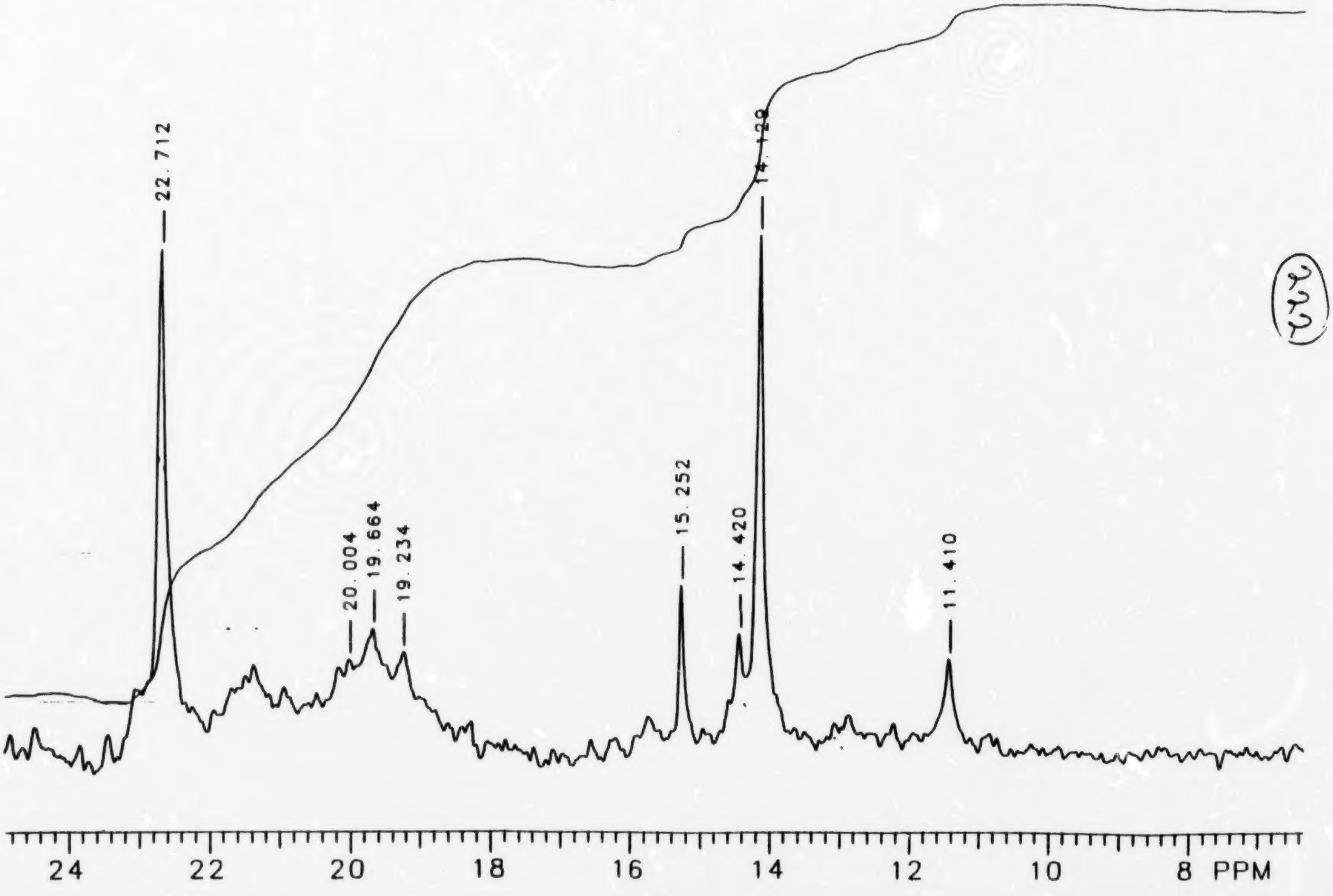
IS=10000

HB6B
$CDCl_3$
IS=1000



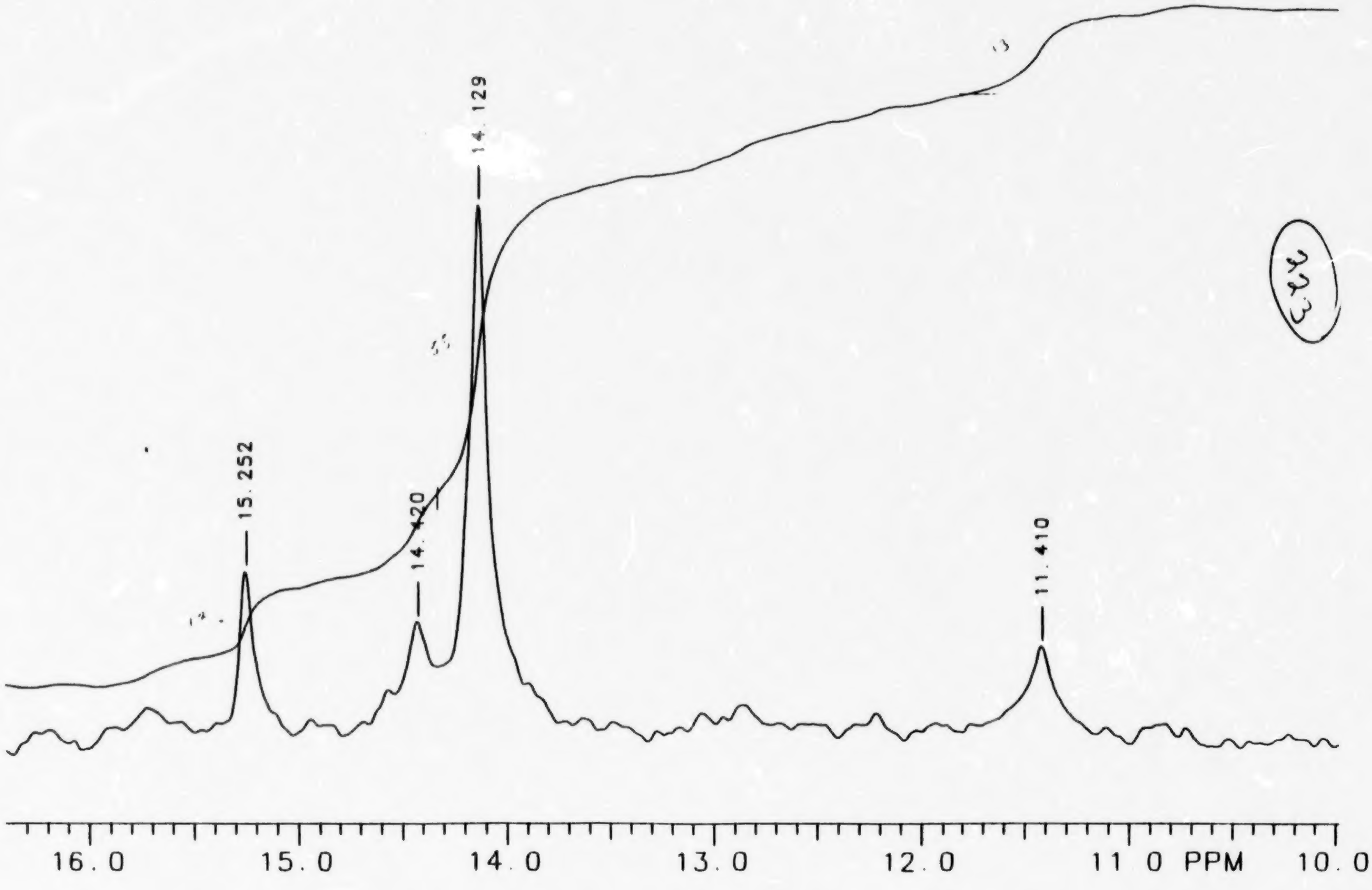
15 - 800

HB6B
$CDCl_3$
IS = 800



HB6B
$CDCl_3$

223

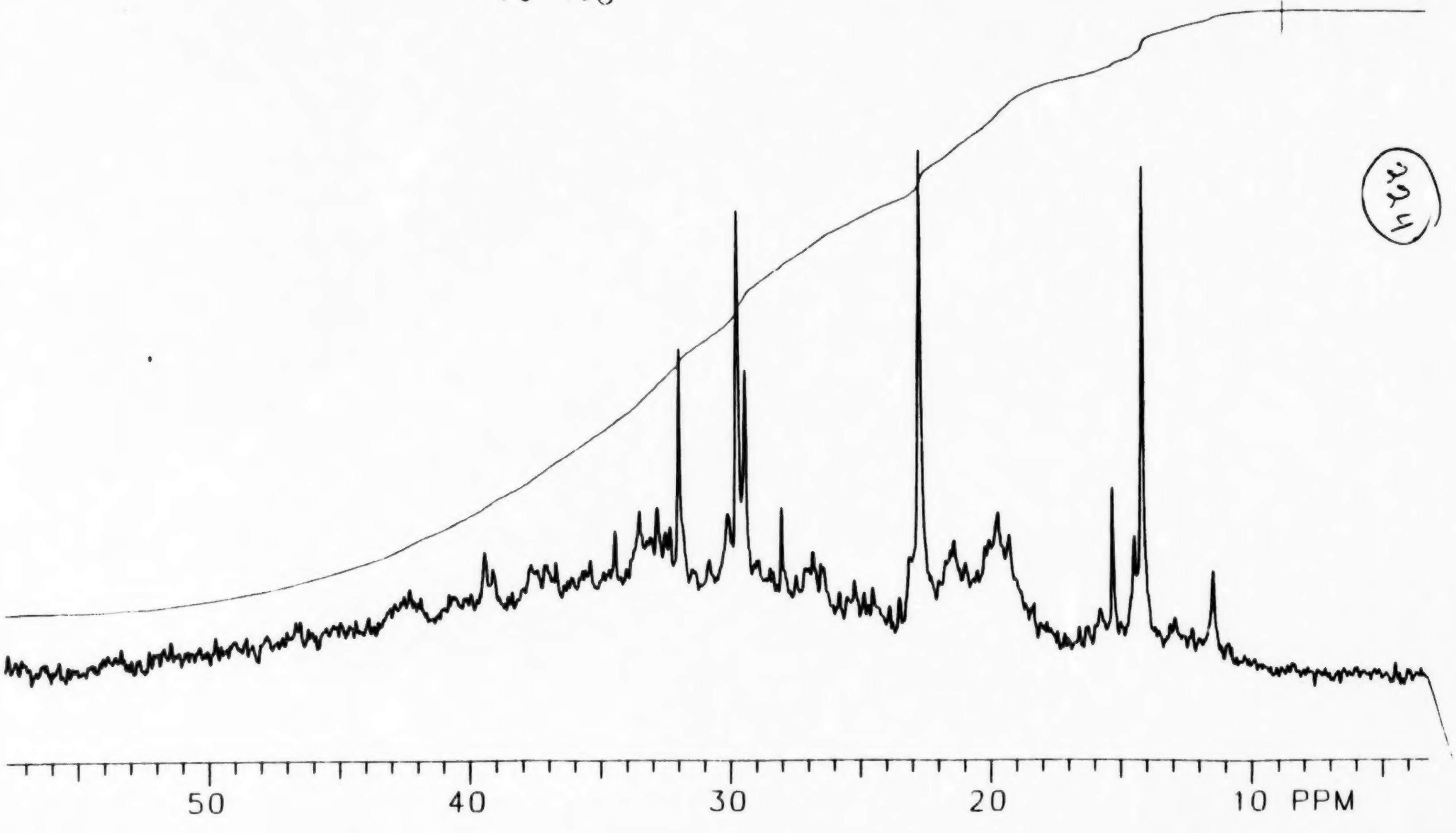


15 = 100

H 13 6 B

$CDCl_3$

IS-100



IS = 300

H B 6 B

CDCl3

IS = 300

(225)